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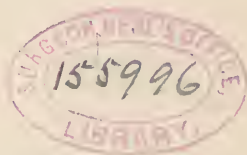




QUALITATIVE  
CHEMICAL ANALYSIS:

A  
GUIDE IN THE PRACTICAL STUDY OF CHEMISTRY  
AND IN  
THE WORK OF ANALYSIS.

BY  
ALBERT B. PRESCOTT, Ph.D.,  
AND  
OTIS C. JOHNSON, M.A.



FOURTH FULLY REVISED EDITION,  
WITH DESCRIPTIVE CHEMISTRY EXTENDED THROUGHOUT.

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## PREFACE TO THE FOURTH REVISED EDITION.

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In this edition the text has been mostly rewritten, to bring in the later results and to agree with fuller experience. The metalloids and acids have received more adequate treatment, and throughout the work the descriptive chemistry has been enlarged, in systematic arrangement. To gain room for these additions, some verbal condensation has been made all through the book, and such matter as could best be spared, including the introductory chapter, has been omitted. With a design to keep within previous limits of size, the edition is only 12 pages larger than the previous one.

In the preface to the first edition it was said to be the chief object in the work "to aid the student in gaining accurate acquaintance with the facts whereby analyses are made, and a clear understanding of the co-ordination of these facts—the principles of analysis." And the authors still believe that the best study of analytical chemistry is among the best of the methods for the study of general chemistry. In this edition, with the purpose to bring together varied resources of analysis for co-operation with each other, to a wider knowledge of chemical reactions, the chief plans for quantitative analysis have been introduced. These are in no case to be resorted to as directions for quantitative operations, which require a strict control of details not presented in this work. With the same purpose, under a like limitation, the leading methods of preparation or of manufacture of compounds are indicated, in order following the statements of "sources" in chemical description.

The special treatment of reactions of oxidation and reduction was introduced by one of the present authors in the third revised edition, and is now extended through the text upon metalloids and acids. The use of negative as well as positive units of valence has been found most helpful for the statement of reactions of oxidation, and is now offered, in its proper notation, where required throughout Part II., but this additional notation will not in the least embarrass readers who would omit it.

The first edition of this work appeared in 1873, the second revised edition in 1876, and the third in 1880. With the first edition were incorporated the Tables for Qualitative Analysis by Professor Silas H. Douglas, editions of which had appeared in 1864, 1865, and 1868. Professor Douglas having some years since retired from engagements in chemistry, and being by his long and most valuable services in chemical education well entitled to release, now withdraws his name from the authorship of this work.

THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN,  
August, 1888.



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# THE NOTATION OF METALLIC COMPOUNDS.

## ACIDS.

An acid is a salt of hydrogen. It consists of an *Acid Radical*,\* united with hydrogen which can be exchanged for a metal, this being the formation of a salt. The hydrogen is the base of the acid, as the metal is the base of the salt. Sulphuric acid, for instance, is sometimes written hydrogen sulphate. *Oxacids* are those whose radicals contain oxygen, as  $\text{HNO}_3$ . *Hydracids* are those whose radicals have no oxygen, as  $\text{HCl}$ ; their names begin with *hydr* and end with *ic*, and the names of their salts end in *ide*. The *Anhydride* of an oxacid is what remains after removing from the acid its basic  $\text{H}$ , and enough  $\text{O}$  to form  $\text{H}_2\text{O}$  with the  $\text{H}$ . Thus, the anhydride of  $\text{H}_2\text{SO}_4$  is  $\text{SO}_3$ , and carbonic anhydride is  $\text{CO}_2$ , carbonic acid being  $\text{H}_2\text{CO}_3$ . Acids whose molecules contain but one atom of basal hydrogen are termed *monobasic*, as  $\text{HNO}_3$  and  $\text{HCl}$ ; those with two atoms of hydrogen in the molecule, *dibasic*, as  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{S}$ ; those with three hydrogen atoms, *tribasic*, as  $\text{H}_3\text{PO}_4$ ; etc. Some of the more important acids are given in the following list :

$\text{HCl}$ ,	hydrochloric	acid, hydrogen chloride, or hydric chloride.
$\text{HClO}_3$ ,	chloric	“ “ chlorate, “ chlorate.
$\text{HBr}$ ,	hydrobromic	“ “ bromide, “ bromide.
$\text{HBrO}_3$ ,	bromic	“ “ bromate, “ bromate.
$\text{HI}$ ,	hydriodic	“ “ iodide, “ iodide.
$\text{HIO}_3$ ,	iodic	“ “ iodate, “ iodate.
$\text{HNO}_3$ ,	nitric	“ “ nitrate, “ nitrate.
$\text{H}_2\text{S}$ ,	hydrosulphuric	“ “ sulphide, “ sulphide.
$\text{H}_2\text{SO}_4$ ,	sulphuric	“ “ sulphate, “ sulphate.
$\text{H}_2\text{SO}_3$ ,	sulphurous†	“ “ sulphite,† “ sulphite.†
$\text{H}_2\text{CO}_3$ ,	carbonic	“ “ carbonate, “ carbonate.
$\text{H}_2\text{CrO}_4$ ,	chromic	“ “ chromate, “ chromate.
$\text{H}_3\text{PO}_4$ ,	phosphoric	“ “ phosphate, “ phosphate.
$\text{H}_3\text{AsO}_4$ ,	arsenic	“ “ arseniate, “ arseniate.
$\text{H}_3\text{AsO}_3$ ,	arsenious	“ “ arsenite, “ arsenite.
$\text{H}_6\text{Fe}_2(\text{CN})_{12}$ ,	hydroferricyanic	“ “ ferricyanide, “ ferricyanide.
$\text{H}_4\text{Fe}(\text{CN})_6$ ,	hydroferrocyanic	“ “ ferrocyanide, “ ferrocyanide.
$\text{HC}_2\text{H}_3\text{O}_2$ ,	acetic	“ “ acetate, “ acetate.
$\text{H}_2\text{C}_2\text{O}_4$ ,	oxalic	“ “ oxalate, “ oxalate.

\* The term Radical is applied to a group of atoms which retains its integrity while transferred from one molecule to another.

† Oxacids whose names end in *ic* form salts with names ending in *ate*; while those, containing less oxygen, whose names end in *ous*, make salts having names ending in *ite*.

An *acid radical* is the group which remains after removing all of the hydrogen from an acid :  $\text{NO}_3$  is nitric acid radical,  $\text{PO}_4$  is phosphoric acid radical. *Exception*—Some organic acids retain a part of their hydrogen in the radical ; thus, acetic acid radical is  $\text{C}_2\text{H}_3\text{O}_2$ .

### METALS.

Of these the more important are given in this list. The accents indicate *bonds*, valence, or quantivalence :

#### First Group.

<b>Ag'</b>	the base of silver or argentic	salts.
<b>Pb''</b>	“ lead “ plumbic	“
<b>(Hg<sub>2</sub>)''</b>	“ mercurous	“

#### Second Group.

<b>Sn''</b>	the base of	stannous	salts.
<b>Sn<sup>iv</sup></b>	“	stannic	“
<b>Sb'''</b>	“	antimonous	“
<b>Sb<sup>v</sup></b>	“	antimonic	“
<b>As'''</b>	found in arsenious compounds.		
<b>As<sup>v</sup></b>	“ arsenic	“	
<b>Hg''</b>	the base of	mercuric	salts.
<b>Bi'''</b>	“ bismuth or	bismuthous	“
<b>(Cu<sub>2</sub>)''</b>	“	cuprous	“
<b>Cu''</b>	“	cupric	“
<b>Cd''</b>	“ cadmium or cadmic		“

#### Third Group.

<b>Fe''</b>	the base of	ferrous	salts.
<b>(Fe<sub>2</sub>)<sup>vi</sup></b>	“	ferric	“
<b>Cr''</b>	“	chromous	“
<b>(Cr<sub>2</sub>)<sup>vi</sup></b>	“	chromic	“
<b>(Al<sub>2</sub>)<sup>vi</sup></b>	“ aluminium or	aluminic	“
<b>Co''</b>	“	cobaltous	“
<b>(Co<sub>2</sub>)<sup>vi</sup></b>	“	cobaltic	“
<b>Ni''</b>	“ nickel or nickelous		“
<b>Mn''</b>	“	manganous	“
<b>(Mn<sub>2</sub>)<sup>vi</sup></b>	“	manganic	“
<b>Zn''</b>	“ zinc or zincic		“

#### Fourth Group.

<b>Ba''</b>	the base of	barium or baric	salts.
<b>Sr''</b>	“	strontium “ strontic	“
<b>Ca''</b>	“	calcium “ calcic	“

*Fifth Group.*

<b>Mg''</b>	the base of magnesium or magnesian salts.
<b>K'</b>	“ potassium “ potassic “
<b>Na'</b>	“ sodium “ sodic “
<b>(NH<sub>4</sub>)'</b> a radical, the base of ammonium or ammoniac salts.	

If a metal forms two classes of salts, the one having the less number of bonds ends in *ous*, and that having the greater ends in *ic*.

The bonds of acid radicals are shown by the number of atoms of (displaceable) hydrogen which the acid contains—*e.g.*, phosphoric acid, **H<sub>3</sub>PO<sub>4</sub>**; phosphoric acid radical, **(PO<sub>4</sub>)'''**.

NORMAL SALTS.

An *inorganic normal salt* consists of a metal and an acid radical. The whole number of bonds of the metal is equal to the whole number of bonds of the acid radical. Thus in bismuth sulphate, **Bi'''<sub>2</sub>(SO<sub>4</sub>)'₃**, each atom of bismuth has three bonds, making six in all, and each group of the acid radical, **(SO<sub>4</sub>)'**, has two bonds, making six in all, and equal to those of the metal. The equality of the bonds may be easily understood in the following examples of normal salts:

<b>Sn''(NO<sub>3</sub>)'₂</b> ,	stannous nitrate.
<b>Ca''₃(PO<sub>4</sub>)'''₂</b> ,	calcium phosphate.
<b>Ba''(IO<sub>3</sub>)'₂</b> ,	barium iodate.
<b>Bi'''₂(C<sub>2</sub>O<sub>4</sub>)'₃</b> ,	bismuth oxalate.
<b>Bi'''₄(Fe(CN)<sub>6</sub>)₃</b> ,	bismuth ferrocyanide.
<b>K'₂S''</b> ,	potassium sulphide.
<b>Bi'''₂(SO<sub>3</sub>)''</b> ,	bismuth sulphite.

.. As has been stated, if a metal forms two classes of salts, that having the less number of bonds ends in *ous*, and the higher in *ic*: thus, **SnCl₂**, stannous chloride; **SnCl₄**, stannic chloride. In such cases only one name can be used.

On the other hand, if a metal forms only one class of salts, then good usage will permit us to employ either of the three systems of nomenclature, as follows:

**BaSO₄**, barium sulphate, baric sulphate, or sulphate of barium.

**Ag₂S**, silver sulphide, argentic sulphide, or sulphide of silver.

Such names as sulphate of potash for **K₂SO₄**, and sulphate of lime for **CaSO₄**, were formerly admissible, but are now almost obsolete.

In seven instances, as given above **(Hg₂)''**, **(Cu₂)''**, **(Al₂)<sup>vi</sup>**, **(Fe₂)<sup>vi</sup>**, **(Cr₂)<sup>vi</sup>**, **(Co₂)<sup>vi</sup>**, **(Mn₂)<sup>vi</sup>**, the atoms of the metal are always written in pairs, never

singly and never with an odd number of atoms. Thus, ferric chloride is not  $\text{FeCl}_3$ , but  $\text{Fe}_2\text{Cl}_6$ ; and mercurous phosphate is not  $\text{Hg}_3\text{PO}_4$ , but  $\text{Hg}_6(\text{PO}_4)_2$ .\*

### *Second Explanation of the Method of Writing Normal Salts.*

Take as many atoms of the metal as the acid radical has bonds, and as many molecules of the acid radical as the metal has bonds; then reduce to lowest terms. In this way bismuth phosphate would be  $\text{Bi}_3(\text{PO}_4)_3$ , and, reduced to lowest terms,  $\text{BiPO}_4$ . This plan is easier for beginners, but is less scientific and does not so easily explain acid and basic salts.

### ACID SALTS.

An acid salt contains hydrogen, and its bonds must be added to those of the metal. The sum is then equal to the bonds of the acid radical—*e.g.* :

$\text{Na}'_2\text{H}'(\text{PO}_4)'''$	disodium hydrogen phosphate.
$\text{NaH}_2\text{PO}_4$	sodium dihydrogen phosphate.
$\text{Cu}_5\text{H}_2(\text{AsO}_4)_4$	pentacupric dihydrogen tetra-arsenate.
$\text{Fe}_6\text{H}_3(\text{PO}_4)_7$	hexaferrie trihydrogen heptaphosphate.
$\text{Mn}_5\text{H}_2(\text{PO}_4)_4$	pentamanganous dihydrogen tetraphosphate.
$\text{Cu}_8\text{H}_2(\text{PO}_4)_6$	octocupric dihydrogen hexaphosphate.

### BASIC SALTS.

Basic salts contain oxygen or hydroxyl, or both, the bonds of which must be added to those of the acid radical, and the sum will always be equal to the whole number of bonds of the metal.

$\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$	pentazincic hexahydrate dicarbonate.
$\text{Bi}_2\text{O}_2\text{CO}_3$	dibismuth dioxide carbonate.
$\text{Zn}_8\text{O}_5(\text{CO}_3)_3$	octozincic pentaoxide tricarbonate.
$\text{Bi}_6\text{O}_7(\text{CrO}_4)_2$	hexabismuth heptaoxide dichromate.
$\text{Fe}_4\text{O}_5\text{SO}_4$	tetraferrie pentaoxide sulphate.

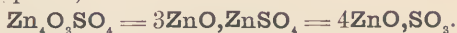
These names are formidable for the beginner, but no other plan seems to indicate by the name the precise composition of the salt.

The *second method*, which is the one more commonly employed, is to consider a basic salt as a combination of a normal salt with an oxide or a hydrate, written consecutively and separated by commas.

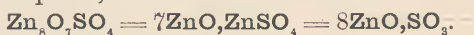
\* From evidences which need not be cited at this stage of study, chemists in general regard the first two as dyads and the other six as tetrads. That is to say, in the cases just mentioned the common structural formulæ of chemists recognize that valence is in exercise between atoms of the same element. Thus ferric chloride is written  $\begin{smallmatrix} \text{Cl} & \text{Cl} \\ \text{Fe} & - & \text{Fe} & \text{Cl} \\ \text{Cl} & \text{Cl} \end{smallmatrix}$ , recognizing iron as  $''' \text{Fe} - \text{Fe} '''$ . And it is to be remembered that molecular formulæ should agree with the molecular weights, which are deduced chiefly from physical constants.

The *third method* is to write the basic salt as an oxide, followed by the anhydride. The three methods may be compared thus :

Tetrazincic trioxide sulphate,



Octozincic heptaoxide sulphate,



Hexabismuth hexaoxide tricarbonate,



### HYDROXIDES.

A Hydroxide is composed of hydroxyl, (OH)', and a metal—*e.g.*, K'OH, Ba''(OH)<sub>2</sub>, Bi'''(OH)<sub>3</sub>.

Formerly hydroxides were called *hydrates*, and, as many authors still use the old name, its occasional use in this work will be understood.

# THE CHEMICAL ELEMENTS.

		ATOMIC WEIGHTS.				ATOMIC WEIGHTS.	
		F. W. Clarke, 1884.	L. Meyer and K. Seubert, 1882.			F. W. Clarke, 1884.	L. Meyer and K. Seubert, 1882.
Aluminium.....	<b>Al</b>	27.009	27.04	Nickel. . . . .	<b>Ni</b>	57.928	58.6
Antimony.....	<b>Sb</b>	119.955	119.6	Niobium.....	<b>Nb</b>	93.812	93.7
Arsenic.....	<b>As</b>	74.918	74.9	Nitrogen.....	<b>N</b>	14.0210	14.01
Barium.....	<b>Ba</b>	136.763	136.86	Norwegium.....	<b>Ng</b>	..... <sup>†</sup>	.....
Beryllium.....	<b>Be</b>	9.085	9.08	Osmium.....	<b>Os</b>	198.494	195.
Bismuth.....	<b>Bi</b>	207.523	207.5	Oxygen.....	<b>O</b>	15.9633	15.96
Boron.....	<b>B</b>	10.941	10.9	Palladium.....	<b>Pd</b>	105.737	106.2
Bromine.....	<b>Br</b>	79.768	79.76	Phosphorus. ....	<b>P</b>	30.958	30.96
Cadmium.....	<b>Cd</b>	111.835	111.7	Platinum.....	<b>Pt</b>	194.415	194.3
Cæsium.....	<b>Cs</b>	132.583	132.7	Potassium.....	<b>K</b>	39.019	39.03
Calcium.....	<b>Ca</b>	39.990	39.91	Rhodium.....	<b>Rh</b>	104.055	104.1
Carbon.....	<b>C</b>	11.9736	11.97	Rubidium.....	<b>Rb</b>	85.251	85.2
Cerium.....	<b>Ce</b>	140.424	141.2	Ruthenium.....	<b>Ru</b>	104.217	103.5
Chlorine.....	<b>Cl</b>	35.370	35.37	Samarium.....	<b>Sm</b>	149.801	.....
Chromium.....	<b>Cr</b>	52.009	52.45	Scandium.....	<b>Sc</b>	43.980	43.97
Cobalt.....	<b>Co</b>	58.887	58.6	Selenium.....	<b>Se</b>	78.797	78.87
Copper.....	<b>Cu</b>	63.173	63.18	Silicon.....	<b>Si</b>	28.195	28.0
Decipium.....	<b>Dp</b>	.....*	.....	Silver.....	<b>Ag</b>	107.675	107.66
Didymium.....	<b>Di</b>	142.121	145.0	Sodium.....	<b>Na</b>	22.998	22.995
Erbium.....	<b>Er</b>	165.891	166.	Strontium.....	<b>Sr</b>	87.374	87.3
Fluorine.....	<b>F</b>	18.984	19.06	Sulphur.....	<b>S</b>	31.984	31.98
Gallium.....	<b>Ga</b>	68.854	69.9	Tantalum.....	<b>Ta</b>	182.144	182.
Germanium.....	<b>Gr</b>	72.324	.....	Tellurium.....	<b>Te</b>	127.960	127.7
Gold.....	<b>Au</b>	196.155	196.2	Terbium.....	<b>Tr</b>	..... <sup>§</sup>	.....
Hydrogen.....	<b>H</b>	1.000	1.	Thallium.....	<b>Tl</b>	203.715	203.7
Indium.....	<b>In</b>	113.398	113.4	Thorium.....	<b>Th</b>	232.020	231.96
Iodine.....	<b>I</b>	126.557	126.54	Tin.....	<b>Sn</b>	117.698	117.35
Iridium.....	<b>Ir</b>	192.651	192.5	Titanium.....	<b>Ti</b>	47.980	50.25
Iron.....	<b>Fe</b>	55.913	55.88	Tungsten.....	<b>W</b>	183.610	183.6
Lanthanum.....	<b>La</b>	138.019	138.5	Uranium.....	<b>U</b>	238.482	239.8
Lead.....	<b>Pb</b>	206.471	206.39	Vanadium.....	<b>V</b>	51.256	51.1
Lithium.....	<b>Li</b>	7.0073	7.01	Ytterbium.....	<b>Yb</b>	172.761	172.6
Magnesium.....	<b>Mg</b>	23.959	23.94	Yttrium.....	<b>Y</b>	88.900	89.6
Manganese.....	<b>Mn</b>	54.855	54.8	Zinc.....	<b>Zn</b>	64.9045	64.88
Mercury.....	<b>Hg</b>	199.712	199.8	Zirconium.....	<b>Zr</b>	89.367	90.4
Molybdenum.....	<b>Mo</b>	95.527	95.9				

The discovery of a few other elements has recently been announced. It is hoped that more accurate investigations will soon place their existence beyond doubt. For list of new elements announced see a report by H. C. Bolton, "Trans. N. Y. Acad. Sciences," Vol. V.

\* Probably 171, Delafontaine.

† Winkler, 1886.

‡ Probably 218.93, Dahll.

§ 148.5, Marignac.



## ORDER OF STUDY.

The order of study of qualitative analysis, in the laboratory under the authors' charge, varied from year to year, is at this time about as follows: Preparatory—a drill in "writing salts," to memorize quantivalence and make the notation familiar. Then, FIRST, a study of the solubilities of metallic salts and hydrates—namely: *A*, obtaining all the precipitates by **potassium hydrate** or **sodium hydrate**, with the metals of successive groups, then the same with **ammonium hydrate**, the student writing equations for all precipitates. *B*, Obtaining the precipitates by potassium **carbonate**, with the successive bases, and formulating the changes. In the same way the students work out the precipitates with, *C*, the **sulphates**; *D*, the **sulphites**; *E*, free **sulphurous acid**; *F*, ammonium **sulphide**; *G*, **hydrosulphuric acid**; *H*, common sodium **phosphate**; *I*, free **phosphoric acid**; *J*, **chlorides**; *K*, **bromides**; *L*, **iodides**; *M*, **iodates**; *N*, potassium **dichromate**; *O*, ammonium **oxalate**. SECOND, a study of the analytical reactions of each base, and then, for the first, practice in the separation of metals from each other, taking them in the order of their groups. THIRD, the analytical reactions of each acid, and then the separations of acids. FOURTH, practice with synthetic operations, devised by the student, for required products, with given materials—equations of all changes being given by the student. Thus, required to make lead sulphide, taking the lead from the metallic state, and the sulphur from calcined sulphate. At this point a full examination is held, and qualification upon all the work passed over is required before going further. FIFTH, the analysis of unknown solid mixtures, each containing from two to seven compounds. The combination of each base, in the greater number, to be determined by the action of solvents upon the mixture. Reports received after analyses of each ten, and results of first and second reports preserved. SIXTH, the analysis of mixtures in solution, mostly involving the action of oxidizing and reducing agents. Lastly, a final examination. There is a daily recitation, with the daily laboratory work.

## PART I.—THE METALS.

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**1. Classification of Metals or Bases.**—In chemical analysis, the metals are commonly divided into **five groups**, according to their deportment, in solution of their salts, with certain general reagents, as follows :

I. Those metals forming *chlorides insoluble* in water are precipitated from the solutions of their salts by the first group reagent, *hydrochloric acid* : **Pb, Ag, (Hg<sub>2</sub>)"**.

II. Metals which are not precipitated by the first group reagent (hydrochloric acid), but are precipitated by the second group reagent, which is *hydrosulphuric acid* slightly acidulated with *hydrochloric acid* : **Sn, Sb, As, Hg"**, **Bi, Cu, Cd, Pb**. Lead chloride is slightly soluble in water ; hence only a part of the lead is precipitated in the first group, and the remainder in the second.

III. Metals which are not precipitated by the first or second group reagents, but by ammonium hydroxide and sulphide in presence of ammonium chloride : **Fe, Cr, Al, Co, Ni, Mn, Zn**.

IV. Those metals which are not precipitated by the first, second, or third group reagents, but by ammonium carbonate in presence of ammonium hydroxide and ammonium chloride : **Ba, Sr, Ca**.

V. Metals which are not precipitated by the reagents of the preceding groups : **Mg, K, Na, NH<sub>4</sub>**.

Only the more common metals are here given. The position of the rarer metals in the five groups is given later.

2. The group reagents of the second group will precipitate the metals of the first group. The group reagents of the third group will precipitate the metals of the first two groups, except **Sn, Sb, and As**, which are soluble in excess of ammonium sulphide. The fourth group reagents will precipitate the metals of the first three groups, except **Ag, Cu, As, Cd, Co, Ni, Zn, Mn**. After filtering out a group precipitate, the reagent which produced it should be added to the filtrate to insure its entire removal, before testing for the next group.



## GROUP V.

3. Magnesium,  $\text{Mg}'' = 23.959 \dots \dots$  An Alkaline Earth Metal.

## The Alkali Metals.

Potassium, . . .	$\text{K}' = 39.019$	Lithium, . . .	$\text{Li}' = 7.0073$
Sodium, . . .	$\text{Na}' = 22.998$	Rubidium, . . .	$\text{Rb}' = 85.251$
Ammonium, . . .	$(\text{NH}_4)'$	Cæsium, . . .	$\text{Cs}' = 132.583$

4. The metals of the alkalies are highly combustible, oxidizing quickly in the air, displacing the hydrogen of water even more rapidly than zinc or iron displaces the hydrogen of acids, and displacing non-alkali metals from their oxides and salts. As elements they are very strong reducing agents, while their compounds are very stable, and not liable to either reduction or oxidation by ordinary means. The five metals, **Cs**, **Rb**, **K**, **Na**, **Li**, present a gradation of electro-positive or basic power, cæsium being strongest, and the others decreasing in the order of their atomic weights, lithium decomposing water with less violence than the others. Their specific gravities decrease,\* their fusing points rise, and as carbonates their solubilities lessen, in the same order. In solubility of the phosphate, also, lithium approaches the character of an alkaline earth.

Ammonium is the basal radical of ammonium salts, and as such has many of the characteristics of an alkali metal. The water solution of the gas ammonia,  $\text{NH}_3$  (an anhydride), from analogy is supposed to contain ammonium hydrate,  $\text{NH}_4\text{OH}$ , known as *the volatile alkali*. Potassium and sodium hydrates are *the fixed alkalies* in common use.

5. The alkalies are very **soluble** in water, and *all the important salts of the alkali metals* (including  $\text{NH}_4$ ) are *soluble* in water, not excepting their carbonates, phosphates (except lithium), and silicates; while *all other* metals form hydrates or oxides, either insoluble or sparingly soluble, and carbonates, phosphates, silicates, and certain other salts quite insoluble in water.

Their compounds being nearly all soluble, the alkali metals are *not precipitated* by ordinary reagents, and, with few exceptions, their salts do not precipitate each other. In **analysis**, they are mostly separated from other metals by non-precipitation.

6. In accordance with the insolubility in water of the non-alkali hydrates and oxides, *the alkali hydrates precipitate all non-alkali metals*, except that ammonium hydrate does not precipitate barium, strontium, and calcium. These precipitates are hydrates, except those of mercury, silver, and antimony.

\* Except those of potassium (0.865) and sodium (0.972).

But certain of the non-alkali hydrates and oxides, though insoluble in water, dissolve in solutions of alkalies; hence, when added in excess, *the alkalies redissolve the precipitates they at first produce with salts of certain metals*, viz.: the hydrates of **Pb**, **Sn**, **Sb**, **Zn**, **Al**, and **Cr** dissolve in the fixed alkalies; and oxide of **Ag** and hydroxides of **Cu**, **Zn**, **Co**, and **Ni** dissolve in the volatile alkali.

### Precipitations by Alkali Hydroxides (**KOH**, **NaOH**, and **NH<sub>4</sub>OH**).

Note the color of the precipitates. For a full statement of the composition of the precipitates, as obtained under different conditions, see the text for the several metals. At certain stages in the addition of alkalies, basic salts of numerous metals are formed. The proportion of hydroxyl is reduced by elevation of temperature, short of that of boiling water, in many instances; thus **Cu(OH)<sub>2</sub>** is changed to **Cu<sub>2</sub>O<sub>2</sub>(OH)<sub>2</sub>**, and at 100° C. to **CuO**.

Barium hydrate,	<b>Ba(OH)<sub>2</sub></b> ,	not caused by <b>NH<sub>4</sub>OH</b> , sol. in 20 parts water.
Strontium	“ <b>Sr(OH)<sub>2</sub></b> ,	“ “ “ 60 “
Calcium	“ <b>Ca(OH)<sub>2</sub></b> ,	“ “ “ 700 “
Magnesium	“ <b>Mg(OH)<sub>2</sub></b> ,	soluble by <b>NH<sub>4</sub>Cl</b> , sol. in 6,000 “
Aluminium	“ <b>Al<sub>2</sub>(OH)<sub>6</sub></b> ,	soluble in excess of fixed alkali hydrates.
Chromium	“ <b>Cr<sub>2</sub>(OH)<sub>6</sub></b> ,	soluble in cold sol. of fixed alkali, precipitated on boiling.
Ferrous	“ <b>Fe(OH)<sub>2</sub></b> ,	slightly soluble by <b>NH<sub>4</sub>Cl</b> . Oxidizes in air.
Ferric	“ <b>Fe<sub>2</sub>(OH)<sub>6</sub></b> ,	
Manganous	“ <b>Mn(OH)<sub>2</sub></b> ,	soluble by <b>NH<sub>4</sub>Cl</b> . Oxidizes in air.
Manganic	“ <b>Mn<sub>2</sub>(OH)<sub>6</sub></b> ,	
Cobalt	“ <b>Co(OH)<sub>2</sub></b> ,	soluble in excess of <b>NH<sub>4</sub>OH</b> , and by <b>NH<sub>4</sub>Cl</b> .
Nickel	“ <b>Ni(OH)<sub>2</sub></b> ,	“ “ “ “
Zinc	“ <b>Zn(OH)<sub>2</sub></b> ,	soluble in both fixed and volatile alkalies.
Copper	“ <b>Cu(OH)<sub>2</sub></b> ,	soluble in <b>NH<sub>4</sub>OH</b> (with blue color).
Cadmium	“ <b>Cd(OH)<sub>2</sub></b> ,	“ “ (colorless).
Bismuth	“ <b>Bi(OH)<sub>3</sub></b> ,	
Lead	“ <b>Pb(OH)<sub>2</sub></b> ,	soluble in excess fixed alkalies.

Silver oxide, **Ag<sub>2</sub>O**, soluble in excess **NH<sub>4</sub>OH**.

Mercurous oxide, **Hg<sub>2</sub>O** (by fixed alkalies).

Mercurous-ammonium chloride, **NH<sub>2</sub>Hg<sub>2</sub>Cl**, from **Hg<sub>2</sub>Cl<sub>2</sub>** by **NH<sub>4</sub>OH**.

**Mercuric oxide**,  $\text{HgO}$  (by fixed alkalies).

**Mercur-ammonium chloride**,  $\text{NH}_2\text{HgCl}$ , from  $\text{HgCl}_2$  by  $\text{NH}_4\text{OH}$ .

**Antimonious oxide**,  $\text{Sb}_2\text{O}_3$ , soluble in excess fixed alkalies.

**Stannous hydrate**,  $\text{Sn}(\text{OH})_2$ ,           “           “           “

**Stannic           “            $\text{Sn}(\text{OH})_4$** ,           “           “           “

7. Solutions of the alkalies are caustic to the taste and touch, and turn red **litmus** blue ; also, the carbonates, acid carbonates, normal phosphates, and some other salts of the alkali metals, give the “alkaline reaction” with test papers. **Sodium nitroferri cyanide**, with hydrogen sulphide, gives a delicate reaction.

8. The hydrates and normal carbonates of the alkali metals are not decomposed by **heat** alone (as are those of other metals), and these metals form the only acid carbonates obtained in the solid state.

9. The fixed alkalies, likewise many of their salts, melt on **platinum** foil in the flame, and slowly vaporize at a bright red heat (distinction from **magnesia**). All salts of ammonium, by a careful evaporation of their solutions on platinum foil, may be obtained in a solid residue, which rapidly vaporizes, wholly or partly, below a red heat (distinction from fixed alkali metals and **magnesium**).

10. The hydrates of the fixed alkali metals, and those of their salts most volatile at a red heat, preferably their chlorides, impart strongly characteristic colors to a non-luminous **flame**, and give well-defined **spectra** with the spectroscope.

#### POTASSIUM. $\text{K} = 39.019$ .

11. Specific gravity 0.865 (GAY-LUSSAC). Fuses at  $62.5^\circ \text{C}$ . (BUNSEN). Boils at  $719^\circ$ – $731^\circ \text{C}$ . (CARNELLEY).

12. **Preparation**.—From the carbonate by fusion with carbon. Also made by electrolysis of the hydroxide. A white metal, brittle at  $0^\circ \text{C}$ ., above that temperature soft like wax. It forms two oxides—the peroxide,  $\text{K}_2\text{O}_2$ , which has no corresponding salts, and potassium oxide,  $\text{K}_2\text{O}$ . The so-called suboxide is a mixture of the oxide and metallic potassium (LUP-**TON**).\*

13. The hydrate, carbonate, dimetallic phosphate, sulphite, nitrite, acetate, and normal tartrate are **deliquescent**.

14. None of the potassium salts are quite **insoluble** in water ; the *platinic chloride*, *acid tartrate*, *silico-fluoride*, *picrate*, *phosphomolybdate*, and *per-chlorate*, being only slightly soluble in water, and quite insoluble in alcohol. The chlorate is but sparingly soluble in cold water, and nearly

\* *Jour. Chem. Soc.*, 1876: 2, 565.

insoluble in alcohol. Also, the carbonate and sulphate are insoluble in alcohol.

15. In ordinary qualitative analysis, **potassium compounds are identified** by their flame-color, using blue glass to exclude the color of the sodium-flame; also by precipitation of potassium acid tartrate in alcoholic acidified solution, or of potassium platinic chloride. Both these precipitations are used in quantitative analysis.

16. **Platinic Chloride ( $\text{PtCl}_4$ )**, added to neutral or acid solutions not too dilute, with hydrochloric acid if the compound be not a chloride, **precipitates potassium platinic chloride,  $(\text{KCl})_2\text{PtCl}_4$** , crystalline, yellow. Non-alkali bases also precipitate this reagent, and if present must be removed before this test. The precipitate is soluble in 19 parts of boiling water, or 111 parts of water at  $10^\circ \text{C}$ . Minute proportions are detected by evaporating the solution with the reagent nearly to dryness, on the water-bath, and then dissolving in alcohol; the yellow crystalline precipitate, octahedral, remains undissolved, and may be identified under the microscope.

17. **Tartaric acid ( $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ )**, or more readily sodium hydrogen tartrate ( **$\text{NaH C}_4\text{H}_4\text{O}_6$** ), precipitates, from solutions sufficiently concentrated, *potassium hydrogen tartrate,  $\text{KHC}_4\text{H}_4\text{O}_6$* , granular-crystalline. If the solution be alkaline, tartaric acid should be added to strong acid reaction. The test must be made in absence of non-alkalin bases. The precipitate is increased by agitation, and by addition of alcohol. It is dissolved by fifteen parts of boiling water or eighty-nine parts water at  $25^\circ \text{C}$ ., by mineral acids, by solution of borax, and by alkalis, which form the more soluble normal tartrate,  **$\text{K}_2\text{C}_4\text{H}_4\text{O}_6$** , but not by acetic acid, or at all by alcohol of fifty per cent.

18. **Picric acid,  $\text{HC}_6\text{H}_2(\text{NO}_2)_3\text{O}$** , precipitates, from solutions not very dilute, the yellow, crystalline *potassium picrate,  $\text{KC}_6\text{H}_2(\text{NO}_2)_3\text{O}$* , insoluble in alcohol, by help of which it is formed in dilute solutions. The dried precipitate detonates strongly when heated.

19. It will be observed that ammonium salts form precipitates with platinic chloride and with tartaric acid, closely resembling those formed with salts of potassium, but the latter is the only fixed alkali which is precipitated by these reagents.

20. Potassium compounds color the **flame violet**. A little of the solid substance, or residue by evaporation, moistened with hydrochloric acid, is brought on a platinum wire into a non-luminous flame. The wire should be previously moistened with hydrochloric acid, and held in the flame until it does not color. The presence of very small quantities of *sodium* enables its yellow flame completely to *obscure the violet* of potassium; but owing to the greater volatility of the latter metal, flashes of violet are sometimes seen on the first introduction of the wire, or at the border of the flame, or in its base, even when enough sodium is present to conceal the violet at full heat.

Silicates may be fused with pure gypsum, giving vapor of potassium sulphate. The interposition of a **blue glass**, or prism filled with indigo solution, sufficiently thick, entirely cuts off the yellow light of sodium, and enables the potassium flame to be seen. The red rays of the *lithium* flame are also intercepted by the blue glass or indigo prism, a thicker stratum being required than for sodium. If organic substances are present, giving luminosity to the flame, they must be removed by ignition. Certain non-alkali bases interfere with the examination.

21. The volatile potassium compounds, when placed in the flame, give a widely-extended continuous *spectrum*, containing two characteristic lines; one line, **K**  $\alpha$ , situated in the outermost red, and a second line, **K**  $\beta$ , far in the violet rays at the other end of the spectrum.

22. **Oxidation.**—Potassium does not oxidize in perfectly dry air. Oxidizes rapidly in moist air, and when thrown upon water bursts into flame. By the aid of heat it reduces the oxides of carbon, phosphorus, and nitrogen to the free elements, and similarly reduces to the metallic state all the oxides of lead, silver, mercury, tin, antimony, arsenic, bismuth, copper, cadmium, zinc, manganese, cobalt, nickel, iron, and the oxides of many of the rarer metals.

### SODIUM. Na = 22.998.

23. Specific gravity .972 (GAY-LUSSAC). Fuses at 95.6° C. (BUNSEN).

**Preparation.**—(1) By igniting the carbonate with carbon; (2) by igniting the hydroxide with metallic iron; (3) by electrolysis.

24. A white, soft metal, resembling potassium in its properties, and, being cheaper, is in greater demand. Sodium forms two oxides, **Na<sub>2</sub>O** and a peroxide, **Na<sub>2</sub>O<sub>2</sub>**.

25. Of ordinary compounds of sodium, only the hydrate, nitrate, and chlorate are **deliquescent**. The carbonate (10 *aq.*), sulphate (10 *aq.*), sulphite (8 *aq.*), phosphate (12 *aq.*), and acetate (3 *aq.*), are efflorescent.

26. The salts of sodium are freely soluble in water, except the metantimoniate and the silico-fluoride, the latter being sparingly soluble.

27. **Sodium is identified** chiefly by its flame-color (30), and by non-precipitation with various reagents. Its soluble salts are weighed in gravimetric operations.

28. Solution of potassium metantimoniate (**KSbO<sub>3</sub>**) produces, in neutral or alkaline solutions, a slow-forming, white, crystalline precipitate, **NaSbO<sub>3</sub>**, almost insoluble in cold water. The reagent must be carefully prepared and dissolved when required, as it is not permanent in solution. (See under Antimonic Acid.)

29. Sodium platinic chloride, (**NaCl**)<sub>2</sub>**PtCl<sub>4</sub>**, crystallizes from its concentrated solutions in red prisms, or prismatic needles (distinction from potassium or ammonium). A drop of the solution to be tested is slightly



acidified with hydrochloric acid from the point of a glass rod on a slip of glass, treated with two drops of solution of platinic chloride, left a short time for spontaneous evaporation and crystallization, and observed under the microscope.

30. Sodium compounds color the **flame** intensely *yellow*—the color being scarcely affected by potassium (at full heat), but modified to orange-red by much lithium, and readily intercepted by blue glass. Infusible compounds may be ignited with calcium sulphate. The test is interfered with by some non-alkali bases.

31. The **spectrum** of sodium consists of a single band, **Na  $\alpha$** , at Fraunhofer's line D, in the yellow of the solar spectrum.

32. The amount of *sodium in the atmosphere*, and in the larger number of substances designed to be "chemically pure," is sufficient to give a distinct but evanescent yellow color to the flame and spectrum.

33. **Oxidation.**—Sodium, in its reducing power, is similar to potassium, but a little less rapid in its action.

#### AMMONIUM.

34. Specific gravity of **NH<sub>3</sub>** gas, 0.5901 (DAVY); of the liquid, 0.6234 (JOLLY). The liquid melts at  $-75^{\circ}$  C. (FARADAY); boils at  $-38.5^{\circ}$  C. (REGNAULT).

35. The anhydride, ammonia (**NH<sub>3</sub>**), *gaseous* at common temperatures, dissolves in twice its weight of cold water, forming a volatile solution lighter than water.

36. The "sesquicarbonate," (**NH<sub>4</sub>**)<sub>2</sub>H<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> (1 *aq.*), or tetra-ammonium dihydrogen tricarbonat, and the phosphate (2 *aq.*), are efflorescent; the nitrate is deliquescent, and the sulphate slightly deliquescent. The normal carbonate is very instable, and used only in solution.

37. The **solubilities** of the *salts* of ammonium correspond very nearly with those of potassium salts.

**Ammonium is found** by obtaining the anhydride, ammonia, in vapor. Precipitation as mercur-ammonium iodide is also used. Ammonium platinic chloride is weighed in quantitative work. For the nitroferri cyanide test, see under Hydrosulphuric Acid.

38. Ammonia gas (**NH<sub>3</sub>**) escapes from its solutions (having alkaline reaction) at ordinary temperatures, more rapidly when heated; and from its combinations, in any mixture (alkaline, neutral, or acid), by heating with an alkali or alkaline earth (potassium or calcium hydrate).



39. *Ammonia gas is recognized*, 1st, by its **odor**; 2d, by turning moistened red **litmus-paper** to blue; 3d, by changing red logwood paper blue; 4th, by rendering paper wet with solution of **cupric sulphate** *blue*;

5th, by *blackening* paper wet with solution of **mercurous nitrate**; 6th, by forming *white fumes* with the **vapors of volatile acids**, vapor of **HCl** forming solid **NH<sub>4</sub>Cl**; vapor of **HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>** forming solid **NH<sub>4</sub> C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>**, etc.

40. A solution of **potassium mercuric iodide**, (**KI**)<sub>2</sub>**HgI<sub>2</sub>**, containing also potassium hydrate—**Nessler's test**\*—produces a brown precipitate of nitrogen dimercuric iodide, **NHg<sub>2</sub>I** (dimercur-ammonium iodide—see under Mercury), soluble by excess of **KI** and by **HCl**; not soluble by **KBr** (distinction from **HgO**):



This very delicate test is applicable to ammonium hydrate or salts; traces forming only a yellow to brown coloration. The potassium mercuric iodide, alone, precipitates the *alkaloids* from *neutral* or *acid* solutions, but does not precipitate ammonium salts from neutral or acid solutions.

41. **Mercuric chloride** (**HgCl<sub>2</sub>**) forms, in solutions of ammonium hydrate or ammonium carbonate, the "white precipitate" of nitrogen dihydrogen mercuric chloride, **NH<sub>2</sub>HgCl**, or mercur-ammonium chloride. If the ammonium is in a salt, not carbonate, it is changed to the carbonate and precipitated, by addition of mercuric chloride and potassium carbonate previously mixed in solutions (with pure water), so dilute as not to precipitate each other (yellow). This test (Bohlig's) is intensely delicate, revealing the presence of ammonia derived from the air by water and many substances.

42. Add a small quantity of recently precipitated and well-washed **silver chloride**, and, if it does not *dissolve* after agitation, then add a little potassium hydrate solution. The solution of the **AgCl**, *before* the addition of the fixed alkali, indicates free ammonia; *after* the addition of the fixed alkali, ammonium salt. (Applicable in absence of thiosulphates, iodides, bromides, and sulphocyanides.)

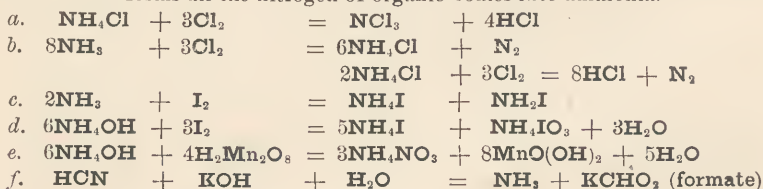
43. **Platinic chloride** and **tartaric acid** form precipitates with ammonium, which, in conditions of production, form and color of crystals, and in solubility, *closely resemble the potassium* precipitates with the same reagent. They may be distinguished by the effect of **ignition**, which, in case of ammonium platinic chloride, leaves pure spongy platinum (without **KCl**), and, in case of ammonium hydrogen tartrate, leaves pure carbon (without **K<sub>2</sub>CO<sub>3</sub>**). Also, **NH<sub>4</sub>H C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>** is more soluble in water than **KH C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>**. *Picric acid* precipitates ammonium, in solutions not very dilute.

44. **Phosphomolybdate of sodium** precipitates ammonium from neutral or acid solutions; also precipitates the *alkaloids*, even from very dilute

\*This reagent may be prepared as follows: To a solution of mercuric chloride add solution of potassium iodide till the precipitate is nearly all redissolved; then add solution of potassium hydrate; leave until the liquid becomes clear, and decant from any remaining sediment.

solutions, and, from concentrated solutions, likewise precipitates **K**, **Rb**, and **Cs** (all the fixed alkalis except **Na** and **Li**).

45. Ammonium salts in solution, treated with *chlorine* gas, generate the instable and violently explosive "nitrogen chloride" ( $\text{NCl}_3$ ?) (*a*). The same product is liable to arise from solid ammonium salts treated with chlorine. Gaseous ammonia, and aqueous ammonium hydrate, with chlorine gas, generate free nitrogen (*b*), a little ammonium chlorate being formed if the ammonia is in excess. *Hypochlorites* or *hypobromites* (or chlorine or bromine dissolved in aqueous alkali, so as to leave an alkaline reaction) liberate, from dissolved ammonium salts, all of their nitrogen (as shown in the second equation of *b*); the measure of the nitrogen gas being a means of quantitative estimation of ammonium.—With *iodine*, ammonium iodide and the explosive iodamides (as in equation *c*) are produced; also, in proportion governed by conditions, iodate (*d*) and hypoiodite may be formed.—Ammonia is liable to atmospheric *oxidation* to ammonium nitrite and nitrate.—*Permanganates* oxidize to nitrate (*e*).—Ammonia is somewhat readily *produced* from nitric acid by strong reducing agents. It is formed with carbonic anhydride, in a water solution of Cyanic acid, and, more slowly, in a water solution of Hydrocyanic acid. It is generated, by fixed alkalis, in boiling solution of Cyanides (*f*); also, in boiling solutions of albuminoids and other nitrogenous organic compounds, this formation being hastened and increased by addition of permanganate (Wanklyn's process). Fusion with fixed alkalis transforms all the nitrogen of organic bodies into ammonia.



46. Heat vaporizes the *carbonate*, and the *haloid salts* of ammonium, *undecomposed*; *decomposes* the *nitrate* with formation of nitrous oxide and water, the *phosphate* and *borate* with evolution of ammonia, and *other salts* with various products.

47. Ammonium compounds impart to the *flame* a faint and evanescent violet color.

LITHIUM = 7.0073.

*Specific gravity*, 0.5936. *Melting point*, 180° C. (356° F.) (BUNSEN).

48. *Occurrence*.—It is a sparingly but widely distributed metal. Usually prepared from lepidolite, triphylene, or petalite. Traces are found in a great many minerals, in mineral springs, and in the leaves and ashes of many plants—*e.g.*, coffee, tobacco, and sugar-cane.

49. *Preparation*.—Salts of the metal were prepared in 1817, and in 1855 Bunsen and Matthiessen isolated it in considerable quantities by electrolysis. It is the lightest metal known; harder than potassium and sodium, but softer than lead. It is volatile at a red heat in an atmosphere of hydrogen;



oxidizes in moist but not in dry, cold air. When thrown upon water, rapidly forms the hydroxide, but does not burst into a flame like sodium and potassium.

**50. Oxide and Hydroxide.**—It forms one oxide ( $\text{Li}_2\text{O}$ ) by heating the metal in oxygen or dry air; cheaper by the action of heat upon the nitrate. The corresponding hydroxide ( $\text{LiOH}$ ) is made by the action of water upon the metal or its oxide; cheaper by heating the carbonate with calcium hydroxide.

**51. Solubilities.**—The chloride, chlorate, and many other salts, are very **deliquescent**. The *carbonate*, *phosphate*, and silico-fluoride are only sparingly **soluble** in water; the other salts of lithium are freely soluble in water, and nearly all soluble in alcohol.

**52. Reactions of Lithium Salts.**—Lithium salts are more fusible and more easily decomposed by fusion than the corresponding potassium and sodium salts.

**53. Sodium phosphate,  $\text{Na}_2\text{HPO}_4$ ,** precipitates trimetallic *lithium phosphate*,  $\text{Li}_3\text{PO}_4$ , soluble in 2,530 parts water; more soluble in solutions of ammonium salts (distinction from magnesium), but much less soluble in strong solution of ammonia. In dilute solutions the precipitate forms only after boiling; and addition of sodium hydroxide to alkaline reaction increases the delicacy of the test, forming a double phosphate of sodium and lithium (C. RAMMELSBURG: *Ann. Phys. Chem.* [2], 7, 157). Its solution in hydrochloric acid is not at once precipitated by ammonium hydrate in the cold (distinction from alkaline earth metals); and the blow-pipe bead of lithium phosphate, with soda, is transparent (that of alkaline earth metals being opaque).

**54. Nitrophenic acid** forms a yellow precipitate, not easily soluble in water.

**55.** Compounds of lithium impart to the **flame** a *carmine-red* color, obscured by sodium, but not by small quantities of potassium compounds. Blue glass, just thick enough to cut off the yellow light of sodium, transmits the red light of lithium; but the latter is intercepted by a thicker part of the blue prism, or by several plates of blue glass.

The **spectrum** of lithium consists of a bright red band,  $\text{Li } \alpha$ , and a faint orange line,  $\text{Li } \beta$ . The color tests have an intensity intermediate between those of sodium and potassium.

**56. Estimation.**—After separation from other elements it may be weighed as a sulphate, carbonate, or phosphate ( $\text{Li}_3\text{PO}_4$ ). It may also be estimated by the comparative intensity of the lines in the spectroscopic (L. BELL: *Amer. Chem. Jour.*, 7, 35).

**57. Oxidation.**—When heated it burns in **Cl, Br, I, S**, and in carbon dioxide.

RUBIDIUM.  $Rb' = 85.251$ .

58. *Specific gravity*, 1.52 (BUNSEN). *Melting point*,  $38.5^{\circ} \text{C}$ . ( $101.3^{\circ} \text{F}$ .) (BUNSEN).

59. **Occurrence.**—Widely distributed in minute quantities; found in lepidolite; in the ashes of some plants; in certain mineral springs, from which source it was first obtained.

60. **Preparation.**—By electrolysis of the chloride, also by heating the carbonate with carbon.

61. **Properties.**—A soft, wax-like metal, with a yellowish tint; inflames when exposed to the air, but less readily than cæsium. It bursts into a flame when thrown upon water; burns when brought in contact with gaseous  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{S}$ , and  $\text{As}$ .

62. **Oxide and Hydroxide.**— $\text{Rb}_2\text{O}$  is supposed to be formed when rubidium burns in oxygen, but it is not yet proven. The corresponding hydroxide ( $\text{RbOH}$ ) is formed when rubidium is oxidized by water, or more cheaply by treating its carbonate with calcium hydroxide.

63. **Reactions of Rubidium Salts.**—Its salts are nearly all soluble. Platinic chloride ( $\text{PtCl}_4$ ) precipitates  $\text{PtRb}_2\text{Cl}_6$ , soluble in 157 parts of water at  $100^{\circ} \text{C}$ ., or 649 parts at  $10^{\circ} \text{C}$ . Tartaric acid precipitates rubidium hydrogen tartrate ( $\text{RbHC}_4\text{H}_4\text{O}_6$ ), soluble in 84 parts of water at  $25^{\circ} \text{C}$ . The spectrum shows two characteristic lines in the violet,  $\text{Rb } \alpha$  and  $\text{Rb } \beta$ , also two others in the red,  $\text{Rb } \delta$  and  $\text{Rb } \gamma$ . The spectrum reaction is so delicate that 0.002 mgrm. may be detected (BUNSEN).

CÆSIUM.  $Cs' = 132.583$ .

64. *Specific gravity*, 1.88 (SETTERBERG). *Melting point*,  $26^{\circ}$  to  $27^{\circ} \text{C}$ . (SETTERBERG).

65. **Occurrence.**—Found in the mineral pollux, and in the water of some springs.

66. **Preparation.**—By electrolysis of the cæsium and barium cyanides. Its reduction by carbon has not yet been accomplished (SETTERBERG).

67. **Properties.**—The metal is silver-white, and soft at ordinary temperatures; oxidizes quickly in the air, and takes fire when thrown on water (SETTERBERG).

68. **Oxide and Hydroxide.**—The oxide formed by burning cæsium in oxygen is supposed to be  $\text{Cs}_2\text{O}$ . The corresponding hydroxide is formed when cæsium is oxidized by water, but prepared cheaper by treating the carbonate with calcium hydroxide or the sulphate with barium hydroxide.

**69. Reactions of Cæsium Salts.**—Nearly all cæsium salts are soluble. Platinic chloride precipitates  $\text{Cs}_2\text{PtCl}_4$  in octahedral crystals, soluble in 235 parts of water at  $100^\circ \text{C}$ ., and in 2,000 parts at  $10^\circ \text{C}$ . Stannic chloride precipitates  $\text{Cs}_2\text{SnCl}_6$ , insoluble in strong hydrochloric acid, but soluble in water. Antimonous chloride precipitates  $\text{CsSbCl}_4$ , completely separating it from all other alkalis (Crooke's *Select Methods*, page 26). Its spectrum consists of two bright blue lines almost coincident with the strontium blue line.

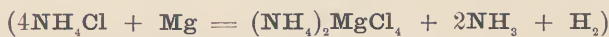
**MAGNESIUM.**  $\text{Mg}'' = 23.959$ .

**70. Specific gravity,** 1.75 (DEVILLE). *Melting point,* about  $500^\circ \text{C}$ . ( $932^\circ \text{F}$ .) (DITTE). *Volatilizes at* about  $1100^\circ \text{C}$ . ( $2507^\circ \text{F}$ .) (DITTE).

**71. Occurrence.**—Magnesite ( $\text{MgCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), brucite ( $\text{Mg}(\text{OH})_2$ ), epsom salts ( $\text{MgSO}_4$ ), and combined with other metals in a great variety of minerals.

**72. Preparation.**—(1) By electrolysis of the chloride. (2) By heating the chloride with potassium or sodium.

**73. Properties.**—A white, hard, malleable, and ductile metal; not acted upon by water or fixed alkali hydroxides at ordinary temperatures, and only slightly at  $100^\circ \text{C}$ . Soluble in acids and in ammonium chloride.



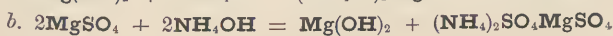
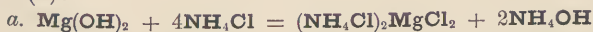
**74. Oxide and Hydroxide.**—Only one oxide of magnesium ( $\text{MgO}$ ) is known with certainty. Formed by burning the metal in the air, and by action of heat upon the hydroxide, carbonate, nitrate, sulphate, oxalate, and other magnesium salts decomposable by heat. The corresponding hydroxide ( $\text{Mg}(\text{OH})_2$ ) is formed by precipitating magnesium salts with the fixed alkalis.

**75. Solubilities.**—The chloride, bromide, iodide, chlorate, nitrate, and acetate (4 *aq.*) are **deliquescent**; the *sulphate* (7 *aq.*), slightly **efflorescent**.

The *hydroxide*, *carbonate*, *phosphate*, and *arseniate* are **insoluble** in water; the *sulphite*, *oxalate*, and *tartrate*, sparingly soluble; the *chromate*, soluble. The hydrate and carbonate are soluble in **ammonium salts**—except ammonium phosphate.

**76. Reactions of Magnesium Salts.**—The **fixed alkali hydrates** and the **hydrates of barium**, strontium, and calcium, precipitate, from magnesium salts in solution, *magnesium hydroxide*,  $\text{Mg}(\text{OH})_2$ , nearly insoluble in water, but soluble in ammonium chloride or sulphate (equation *a*).

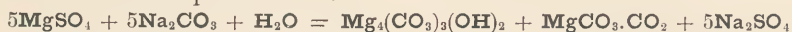
**Ammonium hydroxide** precipitates half the magnesium as a hydroxide, leaving the other half in solution as a double salt of magnesium and ammonium (*b*):



77. Ammonium sulphide forms no precipitate. The normal carbonates of the fixed alkali metals—as  $\text{K}_2\text{CO}_3$ —precipitate *magnesium basic carbonate*,  $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2$ , variable to  $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2$ . Carbonic acid is liberated in the formation of this basic salt :



But in the cold the free  $\text{CO}_2$  combines with another portion of  $\text{MgCO}_3$  to form a soluble supercarbonate :



On boiling, the supercarbonate is precipitated as  $\text{MgCO}_3$  with escape of  $\text{CO}_2$ .

78. Ammonium carbonate scarcely precipitates magnesium salts, except in concentrated solutions, owing to the formation of a soluble double carbonate of magnesium and ammonium :



79. Alkaline phosphates—as  $\text{Na}_2\text{HPO}_4$ —precipitate *magnesium phosphate*,  $\text{MgHPO}_4$ , if the solution be not very dilute. But even in very dilute solutions, by the further addition of ammonium hydroxide (and  $\text{NH}_4\text{Cl}$ ), a crystalline precipitate is slowly formed, *magnesium ammonium phosphate*— $\text{MgNH}_4\text{PO}_4$ . Stirring with a glass rod against the side of the test-tube promotes the precipitation. The addition of ammonium chloride, in this test, prevents formation of any precipitate of magnesium hydrate (76 a). The precipitate dissolves in 15,000 parts pure water, or in 44,000 parts of water containing ammonium hydrate.

80. Alkaline arseniates—as  $\text{Na}_2\text{HASO}_4$ —act with magnesium salts in all respects like the phosphates, giving corresponding precipitates.

81. In the **dry way**, the only characteristic test for magnesium is the *pale rose* color, obtained by igniting, then moistening the compound with solution of **cobalt nitrate**, and again igniting strongly on charcoal. The color is more apparent on cooling, is not intense, and is prevented by presence of many other bases. The spectrum of magnesium, as well as the spectra of most of the metals yet to be described, cannot be obtained by means of the flame, in which their compounds are not volatile. To obtain them, recourse must be had to the electric spark.

82. **Estimation.**—After removal of other metals magnesium is precipitated as  $\text{MgNH}_4\text{PO}_4$ , then changed by ignition to  $\text{Mg}_2\text{P}_2\text{O}_7$  (magnesium pyrophosphate) and weighed as such.

83. **Oxidation.**—Burns brilliantly in the air, giving a light of high actinic power useful in photography. It precipitates the free metals from solutions of **Sb, Mn, Bi, Fe, Zn, Cd, Tl, Sn, Pb, Te, Co, Ni, Cu, Ag, Pt, Pd, Au.**



## GROUP IV.

84. **Alkaline Earth Metals.**—*Barium*,  $Ba'' = 136.763$ . *Strontium*,  $Sr'' = 87.374$ . *Calcium*,  $Ca'' = 39.99$ .

85. **Comparative View.**—Magnesium belongs to the fifth group, and is not usually classified as an alkaline earth; but on account of its close resemblance it is discussed in the following paragraphs.

86. Like the alkali metals, **Ba**, **Sr**, and **Ca** oxidize rapidly in the air at ordinary temperatures—forming alkaline earths—and *decompose water* without the aid of an acid, forming **hydroxides**; also these hydroxides are formed, with evolution of heat, when the oxides are brought in contact with water. **Mg** oxidizes rapidly in the air when ignited, decomposes water at  $100^{\circ} C$ , and its oxide—in physical properties unlike the alkaline earths—slowly unites with water without sensible production of heat. As compounds, these metals are not easily oxidized beyond their quantivalence as dyads, and they require very strong reducing agents to restore them to the elemental state.

87. In *basic power*, **Ba** is the strongest of the four, **Sr** somewhat stronger than **Ca**, and **Mg** much weaker than the other three. It will be observed that the *solubility* of their *hydroxides* varies in the *same* decreasing *gradation*, which is also that of their atomic weights; while the solubility of their *sulphates* varies in a *reverse* order, as follows:

88. The *hydroxide* of **Ba** dissolves in about 20 parts of water; that of **Sr**, in 60 parts; of **Ca**, in 700 parts; and of **Mg**, in 6,000 parts. The *sulphate* of **Ba** is not appreciably soluble in water; that of **Sr** dissolves in 7,000 parts; of **Ca**, in 400 parts; of **Mg**, in 3 parts. To the extent in which they dissolve in water, alkaline earths render their solutions **caustic** to the taste and touch, and alkaline to **test-papers**.

89. The *carbonates*, *normal phosphates*, *silicates*, and some other salts of these four metals, are **insoluble** in water (as are those of the bases of the first three groups). *Magnesium carbonate* is soluble in ammonium salts, whereby its precipitation with the other three is prevented. *Calcium oxalate* and *barium chromate* are insoluble (see table for Group IV.); the oxalates of barium, strontium, and magnesium, and the chromate of strontium, are sparingly soluble; chromate of calcium freely soluble.

In qualitative analysis, the **group-separation** of the fourth-group metals is effected, after removal of the first three groups of bases, by precipitation with carbonate in presence of ammonium chloride, after which magnesium is precipitated from the filtrate, as phosphate.

90. The **hydroxides** of **Ca**, **Sr**, and **Ba**, in their saturated solutions, necessarily dilute, throw down, from solutions of salts of the metals of the first three groups and of **Mg**, thin precipitates of hydrates of the latter

which precipitates are not soluble in excess of the precipitants. In turn, the **fixed alkalis** precipitate, from solutions of **Ba**, **Sr**, **Ca**, and **Mg**, so much of the hydroxides of these metals as does not dissolve in the water present; but *ammonium hydroxide* precipitates only **Mg**, and this but in part, owing to the solubility of  $\text{Mg}(\text{OH})_2$  in ammonium salts.

**91.** Solutions containing **Ba**, **Sr**, **Ca**, and **Mg**, with *phosphoric, oxalic, boracic, or arsenic acid*, necessarily have the acid reaction, as occurs in dissolving phosphates, oxalates, etc., with acids; such solutions are *precipitated by ammonium hydroxide* or by any agent which *neutralizes* the solution, and, consequently, we have precipitates of this kind in the **third group**.



If excess of the ammonium hydroxide be added the precipitate is  $\text{Ca}_3(\text{PO}_4)_2$ . In the case of a magnesium salt the precipitate is  $\text{MgNH}_4\text{PO}_4$ .

**92.** The *carbonates* of the alkaline earth metals are dissociated by heat leaving metallic oxides and carbonic anhydride. This occurs with difficulty in the case of **Ba**, **Sr**, and **Ca**; with readiness in the case of **Mg**; hence **ignition** of the carbonates of **Ba**, **Sr**, and **Ca** causes them to present the alkaline reaction to a slip of moistened litmus-paper.

**93.** Compounds of **Ba**, **Sr**, and **Ca** (preferably with **HCl**) impart characteristic colors to the non-luminous **flame**, and readily present well-defined **spectra**.

**BARIUM.**  $\text{Ba}'' = 136.763$ .

**94.** *Specific gravity*, 3.75 (**KERN**). *Melting-point*,  $475^\circ \text{C}$ . ( $887^\circ \text{F}$ .) (**VAN DER WEYDE**). *Not volatile at a red heat*.

**95. Occurrence**—Found chiefly in heavy spar ( $\text{BaSO}_4$ ) and witherite ( $\text{BaCO}_3$ ).

**96. Preparation**.—(1) By electrolysis. (2) Reduction by potassium or sodium.

**97. Properties**.—A silver-white (**DAVY**) or yellowish-white (**BUNSEN**) metal; ductile, malleable; oxidizes rapidly in the air and in water.

**98. Oxides and Hydroxide**.—The oxide,  $\text{BaO}$ , is formed by the action of heat upon the hydroxide, carbonate, nitrate, oxalate, and all its organic salts. The corresponding hydroxide,  $\text{Ba}(\text{OH})_2$ , is made by treating the oxide with water; is soluble in 20 parts of water at  $15^\circ \text{C}$ , and in 2 parts at  $100^\circ \text{C}$ . The peroxide ( $\text{BaO}_2$ ) is made by heating the oxide almost to redness in oxygen, or air which has been freed from carbon dioxide; by heating the oxide with potassium chlorate (**LIEBIG**) or cupric oxide (**WANKLYN**).

It is used as a source of oxygen, which it gives off at a white heat, **BaO** remaining ; also in the manufacture of hydrogen peroxide, **H<sub>2</sub>O<sub>2</sub>**, which is formed by treating it with dilute acids.



**99. Solubilities.**—Most of the soluble salts of barium are permanent ; the acetate is efflorescent.

The *chloride*, bromide, iodide, sulphides, ferrocyanides, *nitrate*, chlorate, *acetate*, and *phenylsulphate*, are freely soluble in water ; the *carbonate*, *sulphate*, sulphite, *chromate*, *phosphate*, oxalate, iodate, and silico-fluoride, are insoluble in water. The chloride is almost insoluble in strong hydrochloric acid ; likewise the nitrate in strong hydrochloric and nitric acids. The chloride and nitrate are insoluble in alcohol.

**100. Reactions of Barium Salts.**—Barium may be separated from other alkaline earth metals by precipitation as chromate (105), and by its closer precipitation as sulphate (104). The latter precipitation is a sharp distinction from all other metals except lead, strontium, and calcium, and is the operation most used in quantitative analysis of barium and of sulphates.

**101.** The fixed alkali hydroxides precipitate only concentrated solutions of barium salts, as explained by the statement in 88.

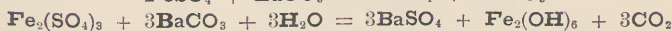
**102.** The alkali carbonates—as **K<sub>2</sub>CO<sub>3</sub>** and **(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>**—precipitate, from barium salts in solution, *barium carbonate* (**BaCO<sub>3</sub>**), white. The precipitation is promoted by heat and by ammonium hydroxide, but is made slightly incomplete by the presence of ammonium chloride and nitrate.

**103. Barium Carbonate**—**BaCO<sub>3</sub>**—is a valuable reagent for special purposes, chiefly for separation of third-group metals. It is used in the form of the moist precipitate, which must be thoroughly washed. It is best precipitated from boiling solutions of chloride of barium and carbonate of sodium or ammonium, washed once or twice by decantation, then by filtration, till the washings no longer precipitate solution of nitrate of silver. Mixed with water to consistence of cream, it may be preserved for some time in stoppered bottles, being shaken whenever required for use. When dissolved in hydrochloric acid, and fully precipitated by sulphuric acid, the filtrate must yield no fixed residue.

This reagent removes sulphuric acid (radical) from all sulphates in solution to which it is added (104).



When salts of non alkali metals are so decomposed, of course, they are left insoluble, as carbonates or hydrates, nothing remaining in solution :



The chlorides of the double triads of the third group, namely, *aluminic*, *chromic*, and *ferric* chlorides, are decomposed by barium carbonate ; while the other metals of the third group, zinc, manganese, cobalt, nickel, and iron in ferrous combination, are not precipitated from their chlorides by this reagent. But tartaric acid, citric acid, sugar, and other organic substances, prevent the decompositions by carbonate of barium.

104. Sulphuric acid ( $\text{H}_2\text{SO}_4$ ), and all soluble sulphates, precipitate *barium sulphate* ( $\text{BaSO}_4$ ), white [88], slightly soluble in hot concentrated sulphuric acid. *Immediate* precipitation by the (dilute) saturated solution of calcium sulphate distinguishes **Ba** from **Sr** (and of course from **Ca**); but precipitation by the (very dilute) solution of strontium sulphate is a more certain test between **Ba** and **Sr**.

105. Normal chromates, as  $\text{K}_2\text{CrO}_4$ , precipitate barium salts (also, strontium salts in solutions not very dilute); the yellow precipitate,  $\text{BaCrO}_4$ , being almost insoluble in water, slightly soluble in acetic acid, but soluble in hydrochloric and nitric acids, and moderately soluble in chromic acid. ( $\text{SrCrO}_4$ , also yellow, is a little more soluble in water than the barium salt.) Dichromates (as  $\text{K}_2\text{Cr}_2\text{O}_7$ ) precipitate barium, as normal chromate, *from the acetate*, in solution not dilute (but do not precipitate strontium).

106. Soluble phosphates, full metallic, or two-thirds metallic, as  $\text{Na}_2\text{HPO}_4$ , precipitate *barium phosphate*, white, consisting of  $\text{BaHPO}_4$  when the reagent is two-thirds metallic, and  $\text{Ba}_3(\text{PO}_4)_2$  when the reagent is full metallic.

107. Oxalates, as  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , precipitate barium from solutions not very dilute; as  $\text{BaC}_2\text{O}_4$ , somewhat soluble in oxalic and acetic acids.

108. Hydro-fluosilicic acid,  $\text{H}_2\text{SiF}_6$ , precipitates white, crystalline  $\text{BaSiF}_6$ , slightly soluble in water, not soluble in alcohol (distinction from strontium and calcium).

109. Solutions of iodates, as  $\text{NaIO}_3$ , precipitate, from barium solutions not very dilute, *barium iodate*,  $\text{Ba}(\text{IO}_3)_2$ , white, soluble in 600 parts of hot or 1,746 parts of cold water (distinction from the other alkaline earth metals).

110. Barium compounds impart to the flame a *yellowish green* color, which appears blue-green when viewed through green glass.

111. The spectrum of barium is at once distinguished from all others by the green bands, **Ba**  $\alpha$ , **Ba**  $\beta$ ; **Ba**  $\gamma$  is less distinct but more characteristic.

112. Estimation.—Barium is weighed as a sulphate, carbonate, or a silico-fluoride ( $\text{BaSiF}_6$ ). It is separated from strontium and calcium: (1) By digesting the mixed sulphates at ordinary temperatures for 12 hours with ammonium carbonate. The calcium and strontium are thus converted into carbonates, which are separated from the barium sulphate by dissolving in hydrochloric acid. (2) By hydro-fluosilicic acid. The hydrate and carbonate are also determined by alkalimetry. One part of a volumetric process recommended depends upon the separation by potassium dichromate in excess of ammonium hydroxide (Crooke's *Select Methods*, page 45).



STRONTIUM.  $\text{Sr}'' = 87.374$ .

113. *Specific gravity*, 2.4 (FRANZ). *Melts at a red heat* (FRANZ).

114. *Occurrence*.—Strontium occurs chiefly in strontianite ( $\text{SrCO}_3$ ) and in celestine ( $\text{SrSO}_4$ ).

115. *Preparation*.—First isolated in 1808 by Davy. Is made by electrolysis; also by fusion of the chloride with sodium amalgam.

116. *Properties*.—A white (DAVY) or faintly yellow metal (FRANZ). It is malleable and ductile; somewhat harder than lead; oxidizes rapidly in air and water.

117. *Oxides and Hydroxide*.—The oxide ( $\text{SrO}$ ) is formed by burning the metal in the air; also by igniting the hydroxide, carbonate, nitrate, oxalate, and all organic strontium salts. The hydroxide is formed by action of water on the oxide. The peroxide,  $\text{SrO}_2$ , is made by treating the hydroxide with hydrogen peroxide ( $\text{Sr(OH)}_2 + \text{H}_2\text{O}_2 = \text{SrO}_2 + 2\text{H}_2\text{O}$ ). It cannot be made, like the corresponding barium peroxide, by heating the hydroxide with oxygen or potassium chlorate (BRODIE).

118. *Solubilities*.—The chloride is slightly *deliquescent*; crystals of the nitrate and acetate *effloresce*.

In *solubility* most compounds of strontium closely resemble those of barium (99)—the *hydrate* being a little less soluble, and the *sulphate* and *chromate* more soluble, in water than the corresponding barium compounds, and the *silico-fluoride* quite soluble (see 88). The chloride is soluble, the nitrate insoluble, in alcohol absolute.

119. *Reactions of Strontium Salts*.—The fixed alkalis precipitate, from concentrated solutions, strontium hydroxide ( $\text{Sr(OH)}_2$ ), soluble in 60 parts of water.

Strontium is *identified*, in the fourth group, after removal of barium, by precipitation with calcium sulphate solution (121); also, quite clearly, by the flame-color and spectrum (122, 123).

120. By its deportment with *carbonates*, *phosphates*, and *oxalates*, strontium is not to be distinguished from barium; the differing reactions of the two metals with *sulphates*, *chromates*, and *hydro-fluosilicic acid* are compared under the head of Barium. Strontium sulphate is soluble in 400 to 500 parts of concentrated nitric or hydrochloric acid.

121. Saturated solution of calcium sulphate ( $\text{CaSO}_4$ ) slowly produces a faint precipitate of  $\text{SrSO}_4$ , prevented or dissolved by presence of hydrochloric and nitric acids, but insoluble in alcohol. It is almost insoluble in a concentrated solution of ammonium sulphate, which separates it from  $\text{CaSO}_4$ .

122. Strontium compounds color the *flame crimson*. In presence of barium the crimson color appears at the moment when the substance, moistened with hydrochloric acid, is first brought into the flame. The paler,

yellowish-red flame of calcium is liable to be mistaken for the strontium-flame.

**123. The spectrum** of strontium is characterized by eight bright bands—namely, six red, one orange, and one blue. The orange line, **Sr  $\alpha$** , at the red end of the spectrum; the two red lines, **Sr  $\beta$**  and **Sr  $\gamma$** , and the blue line, **Sr  $\delta$** , are the most important.

**124. Estimation.**—Strontium is weighed as a sulphate or a carbonate. The carbonate may be determined by alkalimetry. It is separated from calcium by the insolubility of its sulphate in ammonium sulphate. It is separated from barium as stated in 112.

### CALCIUM. $\text{Ca}'' = 39.99$ .

**125. Specific gravity**, 1.57 (BUNSEN). *Melts at a bright red heat* (MATTHIESSEN).

**126. Occurrence.**—Found in the mineral kingdom as a carbonate in marble, limestone, chalk, and arragonite; as a sulphate in gypsum, selenite, alabaster, etc.; as a fluoride in fluor-spar; as a phosphate in apatite, phosphorite, etc. It is found as a phosphate in bones; in egg-shells and oyster-shells as a carbonate. It is found in nearly all spring and river waters.

**127. Preparation.**—By electrolysis; also by fusion with sodium amalgam or with an alloy of sodium and zinc.

**128. Properties.**—Calcium is a pale yellow metal, softer than zinc, but harder than tin and lead. It is malleable and ductile; may be kept for several days in dry air without oxidation, but rapidly oxidizes in moist air and in water.

**129. Oxides and Hydroxide.**—The oxide, **CaO**, is formed by oxidation of the metal in air; by ignition of the hydroxide, the carbonate (limestone), nitrate, oxalate, and all organic acids. Its usefulness when combined with sand, making mortar, is too well known to need any description here. The corresponding hydroxide, **Ca(OH)<sub>2</sub>** (slaked lime), is made by treating the oxide with water. The peroxide, **CaO<sub>2</sub>**, is made by adding hydrogen peroxide to the hydroxide (**Ca(OH)<sub>2</sub> + H<sub>2</sub>O<sub>2</sub> = CaO<sub>2</sub> + 2H<sub>2</sub>O**). It cannot be made by heating the oxide in oxygen or with potassium chlorate (BRODIE).

**130. Solubilities.**—The *chloride, bromide, iodide, nitrate, and chlorate* are **deliquescent**; the acetate is **efflorescent**.

**131.** The *carbonate, oxalate, and phosphate* are **insoluble** in water; the *hydrate, sulphate, sulphite, and iodate* are slightly soluble in water (88), but are insoluble in *alcohol*. The chloride, iodide, and nitrate are soluble in alcohol. The ferrocyanide is soluble, the potassio-ferrocyanide insoluble, in water.

**132. Reactions of Calcium Salts.**—The **fixed alkali hydrates** precipi-

tate *calcium hydrate*,  $\text{Ca}(\text{OH})_2$ , from solutions of calcium salts not very dilute. The precipitate is less soluble in solution of potassium or sodium hydrate, and more soluble in solution of ammonium hydrate than in pure water.

133. In their deportment with soluble **carbonates** (precipitation of  $\text{CaCO}_3$ ) and with alkaline **phosphates** (precipitation of  $\text{CaHPO}_4$  or  $\text{Ca}_3(\text{PO}_4)_2$ ), solutions of calcium cannot be distinguished from solutions of strontium and barium (102, 106).

134. **Sulphuric acid** and soluble **sulphates** (not calcium sulphate) precipitate  $\text{CaSO}_4$  from calcium salts, in moderately concentrated solutions. The precipitate is distinguished from barium and strontium sulphates by dissolving in concentrated solution of *ammonium sulphate*.

135. Alkaline **oxalates**, as  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , precipitate *calcium oxalate*,  $\text{CaC}_2\text{O}_4$ , from even dilute solutions of calcium salts. The precipitate is scarcely at all soluble in *acetic* or *oxalic acids* (separation of oxalic from phosphoric acid), but is soluble in *hydrochloric* and *nitric acids*. The precipitation is hastened by presence of ammonium hydrate. Formed slowly, from very dilute solutions, the precipitate is crystalline, octahedral. If **Sr** or **Ba** are possibly present in the solution tested, an alkaline *sulphate* must first be added, and *after digesting a few minutes*, if a precipitate appears,  $\text{SrSO}_4$ ,  $\text{BaSO}_4$ , or, if the solution was concentrated, perhaps  $\text{CaSO}_4$ , it is filtered out, and the oxalate then added to the filtrate. Observe the precipitate formed by ammonium oxalate in the reagent solution of calcium sulphate. **Ignition** of  $\text{CaC}_2\text{O}_4$  changes it first to  $\text{CaCO}_3$ , then to  $\text{CaO}$ , giving alkaline reaction to test-paper.

136. Neutral alkaline **sulphites**, as  $\text{Na}_2\text{SO}_3$ , precipitate  $\text{CaSO}_3$ , nearly insoluble in water, soluble in hydrochloric or nitric acid, and in sulphurous acid. This reaction is common to the alkaline earths.

137. Alkaline **arsenites** precipitate, from neutral calcium solutions, calcium arsenite,  $\text{CaHAsO}_3$ , soluble in acids and in ammonium hydrate. The precipitate forms slowly. Other alkaline earth metals are not precipitated by arsenites, unless in concentrated solutions.

138. An ammoniacal solution of arsenious acid gives a precipitate of calcium arsenite in neutral calcium salts. Under similar circumstances barium and strontium give no precipitate.

139. Compounds of calcium, preferably the chloride, render the **flame yellowish red**. The presence of strontium or barium obscures this reaction, but a mixture containing calcium and barium, moistened with hydrochloric acid, gives the calcium color on its first introduction to the flame.

140. The **spectrum** of calcium is distinguished by the bright green line,  $\text{Ca } \beta$ , and the intensely bright orange line,  $\text{Ca } \alpha$ , near the red end of the spectrum.

141. **Estimation**.—Calcium is weighed as an oxide, carbonate, or sul-

phate. The carbonate is obtained by precipitating as oxalate, and gently igniting the dried precipitate. The sulphate is precipitated in a mixture of two parts of alcohol to one of the solution.

The best method of separation from strontium, is to treat the nitrates with a mixture of equal volumes of alcohol and ether. The calcium nitrate dissolves, but not more than one part in 60,000 of the strontium is found in the solution. For other methods of separation from barium and strontium see 112 and 124.

### SEPARATION OF THE FOURTH-GROUP METALS.

**142.** Barium, strontium, calcium, and magnesium may be completely precipitated together, either as *carbonates* or as *phosphates*; but a precipitate of phosphates would be intractable in further operations, owing to the difficulty of removing the non-volatile phosphoric acid. Hence, they are precipitated as carbonates, and this could be done by any alkaline carbonate; but the necessity for subsequent examination for fixed alkali metals restricts us to ammonium carbonate. Now, this reagent but imperfectly precipitates magnesium, and from this difficulty, and also because magnesium is more easily separated from alkali metals than from metals of the fourth group, the ordinary scheme of separation provides for the precipitation of **Ba**, **Sr**, and **Ca**, by ammonium carbonate in presence of ammonium chloride, so as to leave **Mg** either with the fifth group, or as a distinct division of the fourth group.

**143.** The precipitation of barium, strontium, and calcium by ammonium carbonate in the presence of chloride, is not as complete as would be desirable in very delicate analyses. For the carbonates of barium, strontium, and calcium are all slightly soluble in ammonium chloride solution; and while the prescribed addition of ammonium hydrate, and excess of ammonium carbonate, greatly reduces the solubility of the precipitated carbonates, yet even with these the precipitation is not absolute, though more nearly so with strontium than with barium and calcium. Thus, in quantitative analyses, if barium and calcium are precipitated as carbonates, it must be done in the absence of ammonium chloride or sulphate, and the precipitate washed with water containing ammonium hydrate.

**144.** But a more accurate precipitation of barium is effected by sulphates, and of calcium by oxalates, and these tests may be applied to portions of the filtrate from the precipitation by carbonates, or of the liquid that has given no precipitate by carbonates. Also, the complete removal of barium and calcium is not only a test for traces of these two metals, but it enables us to accept a slight precipitation of phosphate afterwards as conclusive evidence of the presence of magnesium (unless lithium be present). This precautionary work, done after the ordinary work for barium, strontium, and calcium, may be tabulated as follows:

Divide the filtrate from the fourth group into three portions.

Test in I. for **Ba** with a drop of  $\text{H}_2\text{SO}_4$ , leaving some time.

Test in II. for **Ca** with  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , leaving some time.

If both **Ba** and **Ca** appear, mix I. and II.; let the mixture stand; filter and test the filtrate for **Mg** by  $\text{Na}_2\text{HPO}_4$  and  $\text{NH}_4\text{OH}$ .

If either **Ba** or **Ca** appears, filter it and test the filtrate for **Mg**.

If neither **Ba** nor **Ca** appears, test portion III. for **Mg**.

**145.** The solution of calcium sulphate can be used to distinguish between barium, strontium, and calcium, *provided* that but one metal of the group is present, and that the solution be at least moderately concentrated, and not notably acid.



146. The unlike solubilities in **alcohol**, of the **chlorides** and **nitrates** of barium, strontium, and calcium enable us to separate them quite closely by absolute alcohol, and approximately by "strong alcohol," as follows:

Dissolve the carbonate precipitate in **HCl**, evaporate to dryness on the water-bath, rub the residue to a fine powder in the evaporating dish, and digest it with alcohol. Filter through a small filter, and wash with alcohol.

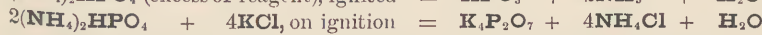
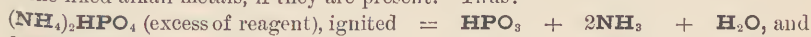
<i>Residue, BaCl<sub>2</sub>.</i>	<i>Filtrate SrCl<sub>2</sub> and CaCl<sub>2</sub>.</i>				
Dissolve in water, test with <b>CaSO<sub>4</sub></b> , etc.	Evaporate to dryness, dissolve in water, change to nitrates by precipitating with <b>(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub></b> , washing, and dissolving in <b>HNO<sub>3</sub></b> . Evaporate the nitrates to dryness, powder, digest with alcohol, filter and wash with alcohol.				
	<table> <tr> <th><i>Residue, Sr(NO<sub>3</sub>)<sub>2</sub>.</i></th><th><i>Filtrate, Ca(NO<sub>3</sub>)<sub>2</sub>.</i></th></tr> <tr> <td>Precipitation by <b>CaSO<sub>4</sub></b> in water solution; flame test, etc.</td><td>Precipitation by <b>H<sub>2</sub>SO<sub>4</sub></b> in alcohol solution; by <b>(NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub></b>, etc.</td></tr> </table>	<i>Residue, Sr(NO<sub>3</sub>)<sub>2</sub>.</i>	<i>Filtrate, Ca(NO<sub>3</sub>)<sub>2</sub>.</i>	Precipitation by <b>CaSO<sub>4</sub></b> in water solution; flame test, etc.	Precipitation by <b>H<sub>2</sub>SO<sub>4</sub></b> in alcohol solution; by <b>(NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub></b> , etc.
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147. Or, the alcoholic filtrate of **SrCl<sub>2</sub>** and **CaCl<sub>2</sub>** may be precipitated with (a drop of) sulphuric acid, the precipitate filtered out and digested with solution of **(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>** and a little **NH<sub>4</sub>OH**. *Residue, SrSO<sub>4</sub>. Solution contains CaSO<sub>4</sub>, precipitable by oxalates.*

## SEPARATION OF MAGNESIUM FROM THE ALKALI METALS.

148. By **ignition** on platinum foil, magnesium compounds do *not vaporize*, as do those of ammonium, *nor melt*, as do many compounds of fixed alkalis. Magnesium is the only one of these metals **precipitated** by ordinary salts—viz., by *phosphates*, carbonates, and hydroxide.

149. The presence of magnesium slightly impairs the delicacy of the *flame-test* for the fixed alkali metals, and entirely prevents their recognition or separation by precipitations. *Phosphate of ammonium* will **remove magnesium** from solution; but, after evaporating the filtrate and igniting its residue, the phosphoric acid remains—combined with the fixed alkali metals, if they are present. Thus:



The residual phosphates of the alkali metals, when moistened with hydrochloric acid, give the flame-tests, but the residue of phosphoric acid obstructs the analysis. The phosphoric acid may be removed by acetate of lead, and the excess of lead by hydrosulphuric acid.

150. A more convenient method of removing magnesium is to precipitate it with solution of **barium hydrate**, and filter, and remove the excess of barium hydrate from the filtrate by addition of sulphuric acid, filtering again.

## GROUP III.

## 151. The Metals of the Earths, and the more Electro-Positive of the Heavy Metals.

Aluminium.....	<b>Al</b>	=	27.009	Didymium.....	<b>D</b>	=	142.121
Chromium.....	<b>Cr</b>	=	52.009	Titanium .....	<b>Ti</b>	=	47.980
Iron.....	<b>Fe</b>	=	55.913	Tantalum.....	<b>Ta</b>	=	182.144
Manganese.....	<b>Mn</b>	=	54.855	Niobium.....	<b>Nb</b>	=	.....
Cobalt.....	<b>Co</b>	=	58.887	Yttrium.....	<b>Y</b>	=	88.900
Nickel.....	<b>Ni</b>	=	57.928	Erbium.....	<b>E</b>	=	165.871
Zinc .....	<b>Zn</b>	=	64.9045	Vanadium.....	<b>V</b>	=	51.256
Uranium.....	<b>Ur</b>	=	238.482	Decipium.....	<b>Dp</b>	=	171. ?
Indium.....	<b>In</b>	=	113.398	Gallium.....	<b>Ga</b>	=	68.584
Beryllium.....	<b>Be</b>	=	9.085	Samarium.....	<b>Sm</b>	=	149.801
Thorium.....	<b>Th</b>	=	232.020	Scandium.....	<b>Sc</b>	=	43.980
Zirconium.....	<b>Zr</b>	=	89.367	Terbium.....	<b>Tr</b>	=	148.5
Cerium.....	<b>Ce</b>	=	140.424	Thallium.....	<b>Tl</b>	=	203.715
Lanthanum..	<b>La</b>	=	138.019	Ytterbium.....	<b>Yb</b>	=	172.761

152. The metals above named gradually oxidize at their surfaces in the air, and their oxides are not decomposed by heat alone. Zinc, iron, cobalt, nickel, and, with more difficulty, manganese, chromium, and most of the other metals of the group, are reduced from their oxides by ignition at white heat with charcoal. They are all reduced from oxides by the metals of the alkalis. Iron is gradually changed from ferrous to ferric combinations by contact with the air. Chromium and manganese are oxidized from bases to acid radicals by ignition with an active supply of oxygen in presence of alkalis; these acid radicals acting as pretty strong oxidizing agents.

153. The *oxides* and *hydroxides* of third-group metals are **insoluble** in water, hence they are precipitated from all their salts by **alkalis**. In the case of *zinc*, the precipitate redissolves in all the alkalis; the *aluminium* hydroxide redissolves in the fixed alkalis, but very slightly in ammonium hydroxide; the precipitate of *chromium* redissolves in cold solution of fixed alkalis, precipitating again on boiling; the hydroxides of *cobalt* and *nickel* dissolve in ammonium hydroxide. The oxides of **Al**, **Cr**, and **Fe**, after ignition, are difficultly soluble by acids.

*The presence of tartaric acid, citric acid, sugar, and some other organic substances, prevents the precipitation of bases of this group by alkalis.*

154. **Salts of ammonium** (as **NH<sub>4</sub>Cl**) dissolve moderate quantities of the hydroxides of manganese, zinc, cobalt, nickel, and ferrous hydroxide; but, so far from dissolving the hydroxide of aluminium, they lessen its slight solubility in ammonium hydroxide.

155. It thus appears that **ammonium hydroxide**, with **ammonium chloride**, the latter necessary on account of magnesium, manganese, and alu-

minium, will fully precipitate only **aluminium**, **chromium**, and **ferrieum** of the important metals named in third group. In many plans of separation these three metals constitute a separate group, and we shall refer to them as Division First of the group.

**156. Ammonium sulphide** precipitates *all* the metals of the third group from neutral or ammoniacal solutions, as follows: The *sulphides* of the group—those of **Fe**, **Mn**, **Co**, **Ni**, and **Zn**—are *soluble in dilute acids*, which acids keep them in solution during the second group precipitation; but are *insoluble in water*, which enables them to be precipitated by alkaline sulphides, and separated from the fourth and fifth groups. The other two metals, **Al** and **Cr**, do not form sulphides, in the wet way, but are precipitated as *hydroxides* by alkaline sulphides.

**157. Hydrosulphuric acid** scarcely precipitates the metals of this group, unless it be from some of their acetates—owing to the solubility of the sulphides in the acids, which would be set free in their formation. Thus, this change cannot occur—



—because the two products would decompose each other. Therefore, neutralized hydrosulphuric acid—a soluble sulphide—is employed for this group, and in a neutral or ammoniacal solution. As most of the *chemically normal* salts of heavy metals have an acid reaction to test-paper, we can only assure ourselves of the requisite neutrality by adding sufficient ammonium hydroxide, which itself precipitates the larger number of the bases, as we have just seen (153). But the resulting precipitate of hydroxide, as **Fe(OH)<sub>3</sub>**, is immediately changed to sulphide, **FeS**, by subsequent addition of ammonium sulphide; as the student may observe, by the alteration in the color of the precipitate.

Ferric and manganic salts are **reduced** to ferrous and manganous salts, by hydrosulphuric acid, in solution, with a *precipitation of sulphur*, and the corresponding reaction occurs with chromates.

**158. Soluble carbonates** precipitate all the metals of this group, in accordance with the general statement for bases not alkali. With aluminium and chromium, the precipitates dissolve sparingly in excess of potassium or sodium carbonate; with zinc, the precipitate dissolves in excess of ammonium carbonate. In the case of ferrous and manganous salts, the precipitates are normal carbonates; with zinc, cobalt, and nickel salts, they are basic carbonates; while with ferric, aluminic, and chromic salts, the precipitates are almost or quite wholly hydroxides. Barium carbonate precipitates the pseudo-triads, which, in the cold and from salts not sulphates, is a separation from the other bases of this group.

**159. Soluble phosphates** precipitate these as they do other non-alkali bases. The acid solutions of phosphates of the metals of the third group are precipitated by neutralization. The recently-precipitated phosphates,



of all the metals of this group which form sulphides, are transformed to sulphides by ammonium sulphide :



Hence, the only phosphates which may occur in a sulphide precipitate are those of **Al**, **Cr**, **Ba**, **Sr**, **Ca**, and **Mg**.

**160.** The metals of the third group are not easily reduced from their compounds to the metallic state by **ignition** before the blow-pipe, even *on charcoal*, except zinc, which then vaporizes. Three of them, however—iron, cobalt, and nickel—are reducible to magnetic oxides. The larger number of them give characteristic colors to **beads** of borax and of microcosmic salt, fused on a loop of platinum wire before the blow-pipe. None of them color the **flame** or give **spectra**, unless vaporized by a higher temperature than that of Bunsen's burner.

### ALUMINIUM. $\text{Al} = 27.009$ .

**161.** *Specific gravity*, 2.583 (MALLET). *Melting point* about  $700^\circ \text{C}$ . ( $1292^\circ \text{F}$ .) (HEEREN).

**162.** *Occurrence*.—Is not found in nature. Is found in corundum, ruby, and sapphire, as nearly pure  $\text{Al}_2\text{O}_3$ ; in diaspore ( $\text{Al}_2\text{O}_3(\text{OH})_2$ ); in bauxite ( $\text{Al}_2\text{O}_3(\text{OH})_4$ ); in felspar ( $\text{K}_2\text{Al}_2\text{SiO}_6$ ); in cryolite ( $\text{Na}_6\text{Al}_2\text{F}_{12}$ ). As a silicate in all clays and in very many minerals. It is widely distributed, constituting about one-twelfth of the earth's crust.

**163.** *Preparation*.—(1) By electrolysis of the fused  $\text{Na}_2\text{Al}_2\text{Cl}_6$ . (2) By fusion of cryolite or the chloride with **Na** or **K**. (3) By heating  $\text{Na}_2\text{Al}_2\text{Cl}_6$  with zinc, with which it forms an alloy from which the zinc is driven off by a white heat. (4) By fusion of the chloride with potassium cyanide. (5) By fusing  $\text{Al}_2\text{S}_3$  with iron. A great many new methods have been patented. Its alloys, especially that with copper, promise extensive usefulness.

**164.** *Properties*.—A tin-white metal; after fusion about as hard as silver, after hammering about as hard as soft iron; very malleable, very ductile, and very sonorous. Its tenacity is nearly equal to that of copper. It conducts electricity eight times better than iron (DEVILLE). The pure metal remains untarnished in the air. Impure specimens become coated with a film of oxide.

**165.** *Oxide and Hydroxide*.— $\text{Al}_2\text{O}_3$  is formed by heating the hydroxide, nitrate, acetate, or other organic salt. It is insoluble in acids after ignition, but may be dissolved after fusion with  $\text{KHSO}_4$  or  $\text{Na}_2\text{CO}_3$ .  $\text{Al}_2(\text{OH})_6$  is formed when aluminium salts are precipitated with cold ammonium hydroxide.  $\text{Al}_2\text{O}_3(\text{OH})_4$  is formed if the precipitation is made at  $100^\circ \text{C}$ .

**166.** *Solubilities*.—The *chloride* and *bromide* are **deliquescent** and in-

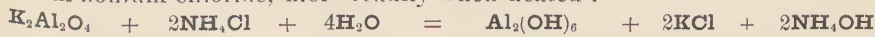
stable. The iodide is known only in solution, the cyanide is not known, the acetate is deliquescent. Aluminium is the most representative constituent of that large class of isomorphous double salts, called **alums**, permanent or slightly efflorescent, as  $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{ aq.}$ , or  $\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24 \text{ aq.}$

The *oxide*, *hydroxide*, and *phosphate* are the principal **insoluble** combinations. Existence of the carbonate is doubtful. The sulphide, made only by heat in the dry way, is decomposed by water. Most insoluble salts of aluminium are changed to soluble compounds by action of fixed alkali hydroxides. In **analysis**, aluminium is obtained in the First Division of Group III., by precipitation, by excess of ammonium hydroxide, with ammonium chloride; then separated from the other members of the First Division by solution with excess of potassium or sodium hydrate (167). Excess of fixed alkali hydrate in boiling solution leaves only aluminium and zinc, of the third-group metals, dissolved, and it is separated from zinc, by non-precipitation with sulphides, and by precipitation with excess of ammonium hydrate.

**167. Reactions of Aluminium Salts.**—The **alkali hydroxides** precipitate *aluminium hydroxide*, grayish-white, gelatinous,  $\text{Al}_2(\text{OH})_6$ , *soluble in fixed alkali hydroxides*, slightly soluble in ammonium hydroxide, though not so if ammonium chloride be present :

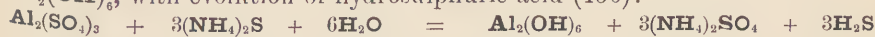


This alkaline solution of aluminium differs from that of zinc, both in not being at all precipitated by boiling, and in being precipitated by excess of ammonium chloride, more readily when heated :



Sufficient ammonium chloride must be added, first to salify the **free** potassium or sodium hydroxide.

**Hydrosulphuric acid** does not precipitate aluminium from any combination; but **ammonium sulphide** precipitates the *aluminium hydroxide*,  $\text{Al}_2(\text{OH})_6$ , with evolution of hydrosulphuric acid (156):



**168. Alkali carbonates** also precipitate the *hydroxide* with evolution of carbonic anhydride—the precipitate being sparingly soluble in excess of sodium or potassium carbonate, scarcely at all soluble in excess of ammonium carbonate :



**Barium carbonate**, on digestion in the cold, precipitates the whole of aluminium from its chloride, as hydroxide mixed with a little basic salt.

\* Or  $\text{Al}_2\text{O}_3(\text{OK})_2$ . A series of volumetric determinations, made by Mr. J. N. Ayres and the author (*Jour. Am. Chem. Soc.*, Feb., 1880), give results according closely with this formula for potassium aluminate, and  $\text{Na}_2\text{Al}_2\text{O}_4$  for sodium aluminate—as fixed by the constituents of the solutions when the precipitates are held dissolved by least excess of alkali.

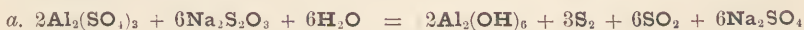
*Basic acetate of aluminium* is precipitated as follows: To the solution of aluminium salt add a little sodium or ammonium **carbonate**, as much as can be added without leaving a precipitate on stirring, then add excess of **sodium or ammonium acetate**, and boil for some time, when the precipitation at length becomes very nearly complete.

169. Alkali **phosphates** precipitate *aluminium phosphate*, white,  $\text{Al}_2(\text{PO}_4)_3$ , soluble in the fixed alkali hydroxides, not in acetic acid.

To separate **Al** from **PO<sub>4</sub>**, fuse the precipitate or powdered substance with  $1\frac{1}{2}$  parts finely divided **silica** and 6 parts dried **sodium carbonate** in a platinum crucible, for half an hour. Digest the mass for some time in water; add **ammonium carbonate** in excess, filter and wash. The residue consists of aluminium sodium silicate; the solution contains the **PO<sub>4</sub>**, as sodium phosphate. The **Al** can be obtained from the residue by dissolving it in **hydrochloric acid**, evaporating to dryness to render the silica insoluble. Treat with hydrochloric acid, and filter; the filtrate containing aluminium chloride.

Also, **Al** (and ferrium) may be separated from **PO<sub>4</sub>** by dissolving in **hydrochloric acid**, adding **tartaric acid** and then **ammonia**, and digesting some time with the mixture of **magnesium sulphate**, **ammonium chloride**, and **ammonium hydroxide**. The filtrate contains most of the aluminium.

170. **Sodium thiosulphate** precipitates, from aluminium salts, in neutral solutions, *aluminium hydroxide*, with free sulphur, and liberation of sulphurous anhydride (*a*) The liquid should be dilute, and boiled till it no longer gives the odor of sulphur dioxide. This precipitation (Chancel's) is a separation from iron. If phosphates are present, and sodium acetate with acetic acid to acidify slightly, the aluminium is precipitated as *phosphate*.



**Potassium ferrocyanide** very slowly precipitates a white mixture of *aluminium hydroxide* and *ferrous cyanide* with formation of hydrocyanic acid. Ferrieyanides do not precipitate aluminium; neither do oxalates. Solution of **borax** precipitates an acid aluminium borate, quickly changed to *aluminium hydroxide*. In very concentrated solutions, addition of **potassium sulphate** causes the crystallization of alum, *potassium aluminium sulphate*, in regular octahedrons or cubes.

171. Compounds of aluminium are not reduced to the metal, but most of them are reduced to the oxide, by **ignition** on charcoal. If now this residue is moistened with solution of **cobaltous nitrate**, and again strongly ignited, it assumes a *blue* color. This test is conclusive only with infusible compounds, and applies only in absence of colored oxides.

172. **Estimation**.—Aluminium is invariably weighed as the oxide, after ignition. It is separated from zinc as a basic acetate; from chromium by oxidizing the latter to chromic acid, by boiling with potassium chlorate and nitric acid, or by fusing with **KNO<sub>3</sub>** and **Na<sub>2</sub>CO<sub>3</sub>**, or by action of **Cl** or **Br** in presence of **KOH**, and after acidulating with **HCl** precipitating the aluminium with ammonium hydroxide. It may be separated from iron by the thiosulphate process; also by precipitation with ammonium sulphide after adding tartrate of potassium and excess of ammonium hydroxide (CARNOT).

**173. Oxidation.**—Pure aluminium does not dissolve in nitric acid. It dissolves very slowly in cold sulphuric acid, evolving hydrogen, and if hot evolving sulphur dioxide. It dissolves in  $\text{HCl}$  and in solution of  $\text{KOH}$ , but molten  $\text{KOH}$  has no action on it. It reduces solutions of  $\text{Pb}$ ,  $\text{Ag}$ ,  $\text{Hg}$ ,  $\text{Sn}$  (Bi incompletely),  $\text{Cu}$ ,  $\text{Cd}$ ,  $\text{Fe}$ ,  $\text{Co}$ ,  $\text{Ni}$  ( $\text{Zn}$  in alkaline solution only),  $\text{Te}$ ,  $\text{Se}$ ,  $\text{Au}$ , and  $\text{Pt}$  to the metallic state.  $\text{As}$  becomes  $\text{AsH}_3$  with alkalies and acids,  $\text{Sb}$  becomes  $\text{SbH}_3$  with acids, but with alkalies becomes metallic antimony. Compounds of  $\text{Mn}$  having more than two bonds are reduced to the dyad. Chromic acid is changed to a chromic compound. It also reduces very many acids.

### CHROMIUM. $\text{Cr} = 52.009$ .

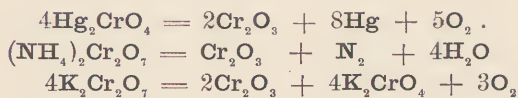
**174. Specific gravity varies, according to method of preparation, from 5.9 (RICHTER) to 7.3 (BUNSEN). Melting point above that of platinum (DEVILLE).**

**175. Occurrence.**—Not found native. It is found in several minerals. Chrome-ironstone or chromite ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) is the chief ore of chromium, and is usually employed in the manufacture of chromium compounds.

**176. Preparation.**—(1) By electrolysis of the chloride. (2) By fusing the chloride with potassium or sodium. (3) By ignition of the oxide with carbon. (4) By fusing  $\text{Cr}_2\text{Cl}_6$  with zinc, using  $\text{KCl}$  and  $\text{NaCl}$  as a flux, and removing the excess of zinc by dissolving it in nitric acid, which does not dissolve metallic chromium.

**177. Properties.**—A light-green, crystalline, and almost infusible powder. .5 to .75 per cent. renders steel harder and improves its quality.

**178. Oxide and Hydroxide.**—Chromous oxide ( $\text{CrO}$ ) has not been isolated. The corresponding hydroxide  $\text{Cr}(\text{OH})_2$  is made by treating  $\text{CrCl}_2$  with  $\text{KOH}$ . Chromic oxide ( $\text{Cr}_2\text{O}_3$ ) is made by a great variety of methods, among which are fusing the nitrate, or higher or lower oxides and hydroxides in the air; heating mercurous chromate, or the dichromates of the alkalies.



In the last the  $\text{K}_2\text{CrO}_4$  may be separated by water. After heating to redness  $\text{Cr}_2\text{O}_3$  is insoluble in acids. Chromic hydroxide is precipitated by adding  $\text{NH}_4\text{OH}$  to chromic solutions. That formed by precipitating with  $\text{KOH}$  or  $\text{NaOH}$  retains traces of the alkali, not easily removed by washing. In addition to chromic acid ( $\text{H}_2\text{CrO}_4$ ) a per-chromic acid, supposed to be  $\text{HCrO}_5$ , is formed when  $\text{H}_2\text{CrO}_4$  is treated with peroxide of hydrogen ( $\text{H}_2\text{O}_2$ ).

**179. Reactions of Chromous Salts.**—Chromous chloride ( $\text{CrCl}_2$ ) is



formed by dissolving the metal in  $\text{HCl}$ , or by gently heating  $\text{Cr}_2\text{Cl}_6$  in hydrogen gas. The blue solution formed by treating a solution of  $\text{Cr}_2\text{Cl}_6$  with zinc contains  $\text{CrCl}_2$  (*J. Pr. Chem.*, 90, 12). It is a strong reducing agent, oxidizing rapidly when exposed to the air. From its solution  $\text{KOH}$  and  $\text{NaOH}$  precipitate  $\text{Cr}(\text{OH})_2$ . Precipitates are formed by  $\text{NH}_4\text{OH}$ , by soluble carbonates, sulphides, sulphites, etc.

**180. Solubilities of Chromic Salts.**—There are two modifications of chromic salts, one having a green color and the other violet to red. There are many double salts. The chloride is **deliquescent**.

*Chromic oxide*, *hydroxide*, and *phosphate* are **insoluble** in water. The carbonate and sulphide are not formed in the wet way. There are modifications of the chloride and sulphate insoluble in water. In **analysis**, chromium is precipitated in the third group as a hydroxide, and identified by the oxidation of this hydroxide to a salt of chromic acid, known by its colored precipitates with lead and barium salts. It is separated in the First Division of the group.

**181. Reactions of Chromic Salts.**—The **fixed alkali hydroxides**, as,  $\text{KOH}$ , precipitate the bluish-green *chromic hydroxide*,  $\text{Cr}_2(\text{OH})_6$ . Other hydroxides are formed in certain conditions. The precipitate redissolves readily in excess of the alkalis while cold, the green solution being  $\text{K}_2\text{Cr}_2\text{O}_7$ .

Long boiling reprecipitates the whole of the chromium, as hydroxide; the same result is effected on heating by addition of ammonium chloride. (Compare 167, last equation.)

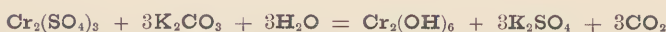
**Ammonium hydroxide** precipitates *chromic hydroxide*, which but slightly redissolves with excess of the alkali in the cold and all reprecipitates readily on heating. The precipitate from solutions of green chromic salts is grayish green, dissolving with acids to form a green solution again; from solutions of violet chromic salts the precipitate is grayish-blue, dissolving with acids to reproduce the violet solution. The tints are, however, modified by the degree of concentration of solution, and by other conditions.

**182.** Hydrosulphuric acid does not affect solutions of chromic salts, whether acid, neutral, or alkaline, and **ammonium sulphide** precipitates *the hydroxide* with evolution of hydrosulphuric acid. The equation corresponds to that for aluminium (167).

Both hydrosulphuric acid and ammonium sulphide, acting on **Chromic Acid** or chromates, abstract oxygen and form the chromic base. In the neutral solution for the third-group precipitation this deoxidation leaves the chromium in the precipitate as a hydrate; whence it is that the occurrence of chromium in the third group of bases, as frequently as otherwise, must be referred to the existence of combinations of chromic acid in the material examined. (See 194 a.)

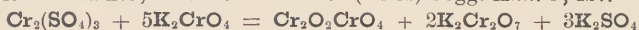
**183.** Alkali **carbonates** precipitate chromium *hydroxide*, nearly free

from carbonate, somewhat soluble in excess of potassium or sodium carbonate :



**Barium carbonate** precipitates chromium from its solutions (better from the chloride) as a hydrate with some basic salt, the precipitate being complete after long digestion in the cold. For removal of excess of reagent, add  $\text{H}_2\text{SO}_4$  and the filtrate will contain the chromium as a sulphate.

**184. Soluble phosphates**—as  $\text{Na}_2\text{HPO}_4$ —precipitate *chromic phosphate*,  $\text{Cr}_2(\text{PO}_4)_2$ , insoluble in acetic acid. **Cyanide of Potassium** precipitates the hydroxide. **Ferrocyanides**, and **oxalates**, cause no precipitates. **Potassium chromate** colors an acid solution of chromic salt brown-yellow ; on addition of ammonium hydroxide, a precipitate of the same color is obtained, chromic chromate. (MAUS) Pogg. Ann. 9, 127.



**185.** Chromic oxide and chromic salts dissolve in **beads of microcosmic salt**, and of borax, before the blow-pipe, in both reducing and oxidizing flames, with a yellowish-green tint while hot, becoming emerald-green when cold.

**186. Estimation.**—Chromium is weighed as an oxide. It is brought into this form either by precipitation as a hydroxide and ignition, or by simple ignition. It may, however, be changed to a chromate, and estimated as such.

**187. Oxidation.**—Metallic chromium does not dissolve in  $\text{HNO}_3$ , but quickly dissolves in  $\text{HCl}$ , forming  $\text{CrCl}_3$ , which is a strong reducing agent, changing  $\text{HgCl}_2$  to  $\text{Hg}_2\text{Cl}_2$ ,  $\text{CuSO}_4$  to  $\text{Cu}$ ,  $\text{SnCl}_2$  to  $\text{Sn}$ , etc.

Chromic compounds in alkaline mixture are oxidized to chromates by reducing  $\text{PbO}_2$  to  $\text{PbO}$ ,  $\text{Ag}_2\text{O}$  to  $\text{Ag}$ ,  $\text{Hg}_2\text{O}$  and  $\text{HgO}$  to  $\text{Hg}$ ,  $\text{CuO}$  to  $\text{Cu}_2\text{O}$ ,  $\text{K}_2\text{Mn}_2\text{O}_8$  to  $\text{MnO}_2$ ; also by  $\text{Cl}$ ,  $\text{Br}$ , and  $\text{I}$  forming a chloride, bromide, or iodide. A chromate is formed when, in the presence of  $\text{Na}_2\text{CO}_3$ , any chromic compound is fused with  $\text{KNO}_3$ ,  $\text{KClO}_3$ ,  $\text{KBrO}_3$ , or  $\text{KIO}_3$ ;  $\text{NO}$  and a chloride, bromide, or iodide being produced.

### CHROMIC ACID.

**188.** Chromic anhydride,  $\text{CrO}_3$ , commonly called “chromic acid,” is a scarlet-red solid, usually in acicular crystals, very deliquescent in the air, and soluble in a small proportion of water. It is a very powerful oxidizing agent, acting explosively with combustible substances, and as a caustic to living tissues. Its soluble salts are poisonous, and have a bitter metallic taste.

**189.** The alkali metals form yellow **normal chromates** and reddish **dichromates**; most other metals form normal chromates, yellow or red; a few form only basic or instable chromates. Most soluble salts of chromic acid crystallize in **permanent** forms; sodic normal chromate is efflorescent.

**190.** All the chromates of the alkali metals, and those of magnésium,

calcium, zinc, and copper, are **soluble** in water; strontium and mercuric chromates sparingly soluble; barium, manganous, bismuth, mercurous, silver, and lead chromates **insoluble** in water. Nitric acid transposes chromates.

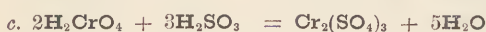
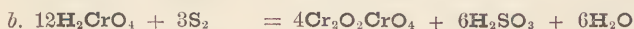
**191. Lead salts** precipitate, from normal and from superchromates, the yellow, *lead chromate*,  $\text{PbCrO}_4$ , slowly soluble in nitric acid, not soluble in acetic acid, difficultly soluble in potassium hydrate.

**192. Barium salts** precipitate from solutions of normal chromates, also from concentrated solutions of superchromates, the normal *barium chromate*, yellow, soluble in hydrochloric and nitric acids, slightly soluble in chromic acid (105).

**193. Silver salts** precipitate *silver chromate*,  $\text{Ag}_2\text{CrO}_4$ , dark red, soluble in nitric acid and in ammonia. **Mercurous nitrate** precipitates *mercurous chromate*,  $\text{Hg}_2\text{CrO}_4$ , dark red, decomposed by ignition into chromic oxide, oxygen, and vapor of mercury (178).

**194.** Chromic anhydride and chromates are DEOXIDIZED TO CHROMIC compounds by various **reducing agents**. The following instances occur frequently in qualitative analysis: other examples are given, in the study of Chromate reductions.

**Hydrosulphuric acid**, in acid solutions, quickly causes reduction to a green chromic salt solution (*a*). At first the sulphur is all precipitated, white in the green liquid; but on warming, it slowly dissolves by oxidation to sulphurous acid, with precipitation of brown basic chromate (*b*), the action being continued, with slow oxidation of the sulphurous acid (*c*) [H. B. Parsons]. **Ammonium sulphide**, in solutions neutral or alkaline, precipitates *chromic hydrate*, green, with oxidation of the sulphide. The precipitate is liable to contain sulphur. In case of yellow or supersulphide of ammonium, it is stated that thiosulphate is obtained in the solution (*d*).



**195.** By **ignition** on charcoal the carbon deoxidizes chromic anhydride, free or combined, and a *green mass*,  $\text{Cr}_2\text{O}_3$ , is left. Chromates give, in the **beads**, the results described for chromic base in 185. For a more complete statement of the oxidizing action of this acid see under chromic acid, Part II.

#### IRON. Fe = 55.913.

**196.** *Specific gravity variable; reduced by electricity* 8.1393 (SMITH); *by hydrogen* 8.007 (SCHIFF); *by carbon* 7.130 (PLAYFAIR). *Melting-point, gray cast*, 1275° C. (2327° F.) (LEDEBUR); *cast steel*, 1375° C. (2507° F.) (BLOXAM).

**197. Occurrence.**—Native iron is rarely found except in meteorites. The chief ores of iron are red hematite or specular iron ore ( $\text{Fe}_2\text{O}_3$ ), brown hematite ( $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ), magnetic iron ore ( $\text{Fe}_3\text{O}_4$ ), iron pyrites ( $\text{FeS}_2$ ),



spathic iron ore ( $\text{FeCO}_3$ ), clay iron-stone ( $\text{FeCO}_3$  with clay), black band ( $\text{FeCO}_3$  mixed with bituminous matter).

**198. Preparation.**—Pure iron is not usually found in the market. It is made : (1) by electrolysis ; (2) by heating its purified salts with hydrogen ; (3) by heating the purified salts with some form of carbon ; (4) in metallurgy it is made from the ores, and the reducing agent is coal, charcoal, and, more recently, natural gas.

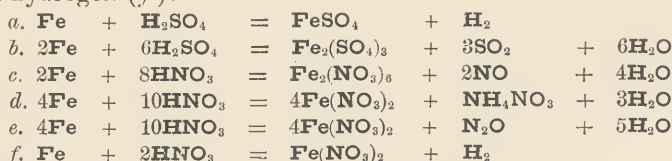
**199. Properties.**—Pure iron is the most tenacious of all the metals except cobalt and nickel. It softens at a red heat, may be welded at a white heat, but above the melting point is brittle under the hammer. Finely divided iron burns in the air when ignited. When made by (2) it is a very fine powder, and if made at as low a temperature as practicable, it takes fire spontaneously when exposed to the air. Steel contains from 0.2 to 1.5 per cent. of carbon, while cast iron contains from 2 to 5 per cent. Pure iron is attracted by the magnet, but does not retain its magnetism. Permanent magnets are made of steel. All the ordinary properties of iron are too well known to need any description.

**200. Oxides and Hydroxides.**—*Ferrous oxide* ( $\text{FeO}$ ) is made from  $\text{Fe}_2\text{O}_3$  by heating it to  $300^\circ \text{C}$ . in an atmosphere of hydrogen ; also by heating  $\text{Fe}_2\text{C}_2\text{O}_4$  to  $160^\circ \text{C}$ ., air being excluded. It takes fire spontaneously in the air, oxidizing to  $\text{Fe}_2\text{O}_3$ . Ferrous hydroxide,  $\text{Fe}(\text{OH})_2$  is formed by precipitating ferrous salts with  $\text{KOH}$  or  $\text{NaOH}$ , perfectly white when pure, but frequently green from partial oxidation. Ferric oxide,  $\text{Fe}_2\text{O}_3$ , is formed by heating  $\text{FeO}$ ,  $\text{Fe}(\text{OH})_2$ , or any ferrous salt consisting of a volatile or organic acid in the air ; more rapidly by heating  $\text{Fe}_2(\text{OH})_6$ ,  $\text{Fe}_2(\text{NO}_3)_6$ , or  $\text{Fe}_2(\text{SO}_4)_3$ . Ferric hydroxide is formed by precipitating cold dilute ferric salts with alkalis or alkali carbonates, and drying at  $100^\circ \text{C}$ . If  $\text{KOH}$  or  $\text{NaOH}$  is used, the precipitate requires longer washing than when  $\text{NH}_4\text{OH}$  is employed. By increasing the temperature and concentration of the solutions the following definite compounds may be formed :  $\text{Fe}_2\text{O}_2(\text{OH})_2$ ,  $\text{Fe}_2\text{O}(\text{OH})_4$ ,  $\text{Fe}_4\text{O}_5(\text{OH})_2$ ,  $\text{Fe}_4\text{O}_3(\text{OH})_6$ ,  $\text{Fe}_6\text{O}_4(\text{OH})_{10}$  (hexaferric-tetroxide-dekahydroxide).  $\text{Fe}_3\text{O}_4$  is slowly formed by heating  $\text{FeO}$  or  $\text{Fe}_2\text{O}_3$  to a white heat. Its corresponding hydroxide may be made by precipitation,  $\text{FeCl}_2 + \text{Fe}_2\text{Cl}_6 + 8\text{NH}_4\text{OH} = \text{Fe}_3(\text{OH})_8 + 8\text{NH}_4\text{Cl}$ .  $\text{Fe}_3(\text{OH})_8$  when heated to  $90^\circ \text{C}$ . forms  $\text{Fe}_3\text{O}_4$ . The black color and magnetic properties show that it is a chemical *salt* and not a mechanical mixture of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ .  $(\text{Fe}_2)^{\text{vi}}$  acts as an acid towards the  $\text{Fe}''$  ; this oxide,  $\text{Fe}_3\text{O}_4$ , or  $\text{FeFe}_2\text{O}_4$ , may be called ferrous ferrite. Other ferrites have been formed—*e.g.*, calcium ferrite,  $\text{CaFe}_2\text{O}_4$  (PERCY) ;  $\text{MgFe}_2\text{O}_4$  and  $\text{BaFe}_2\text{O}_4$  (LIST, *Ber.* 1878, 1512) ; zinc ferrite,  $\text{ZnFe}_2\text{O}_4$  (EBELMEN). Compare potassium aluminate ( $\text{K}_2\text{Al}_2\text{O}_4$ ), and potassium chromite ( $\text{K}_2\text{Cr}_2\text{O}_4$ ) (167 and 181).

**201. Ferric Acid**,  $\text{H}_2\text{FeO}_4$ , and its anhydride ( $\text{FeO}_3$ ) have not been isolated. Potassium ferrate ( $\text{K}_2\text{FeO}_4$ ) is made (1) by electrolysis ; (2) by heating

iron filings,  $\text{FeO}$  or  $\text{Fe}_2\text{O}_3$ , to a red heat with  $\text{KNO}_3$ ; (3) by heating  $\text{Fe}_2(\text{OH})_6$  with potassium peroxide  $\text{K}_2\text{O}_4$ ; (4) by passing  $\text{Cl}$  or  $\text{Br}$  into a solution of 5 parts of  $\text{KOH}$  in 8 parts of water in which  $\text{Fe}_2(\text{OH})_6$  is suspended; the temperature should be not above  $50^\circ \text{C}$ . ( $122^\circ \text{F}$ .) It has a purple color; is a strong oxidizing agent. It slowly decomposes on standing ( $4\text{K}_2\text{FeO}_4 + 10\text{H}_2\text{O} = 8\text{KOH} + 2\text{Fe}_2(\text{OH})_6 + 3\text{O}_2$ ). With barium salts it precipitates a stable barium ferrate ( $\text{BaFeO}_4$ ).

**202. Solubility of Iron.**—Iron dissolves, in hydrochloric acid, and in dilute sulphuric acid, to ferrous salts, with liberation of hydrogen (*a*); concentrated cold  $\text{H}_2\text{SO}_4$  has no action, but if hot  $\text{SO}_2$  is evolved and a ferric salt formed (*b*); in moderately dilute nitric acid, with heat, to ferric nitrate, liberating chiefly nitric oxide (*c*); in cold dilute nitric acid, forming ferrous nitrate with production of ammonium nitrate (*d*), of nitrous oxide (*e*), or of hydrogen (*f*):



In dissolving the iron of commerce in hydrochloric acid the carbon which it always contains, so far as combined in the carbide of iron, will pass off in gaseous hydrocarbons, and so far as uncombined will remain undissolved, as graphitoid carbon.

Iron acts as a base in **two kinds of salts**: the ferrous and the ferric; both are stable, in considerable variations of temperature, when undisturbed by other substances; but the ferrous compounds are changed to ferric by contact with the air, and by oxidizing agents generally; while the ferric compounds are permanent in the air, but are changed to ferrous combinations by reducing agents. In the systematic course of analysis, by the treatment necessary in separation from other metals, the ferric compounds are reduced to ferrous compounds, and then, by air and by reagents, partially or wholly changed to ferric compounds again, and the original substance must always be tested for determination, whether ferrous or ferric. The metal oxidizes in moist air to tetraferriic-trioxide-hexahydroxide,  $\text{Fe}_4\text{O}_3(\text{OH})_6$ . By ignition in the air, chiefly ferrous oxide is formed, but by a long-continued white heat  $\text{Fe}_3\text{O}_4$  is formed, see (200). Scale oxide is  $(\text{FeO})_6\text{Fe}_2\text{O}_3$ .

**203. Solubilities of Ferrous Salts.**—**FERROUS** salts, in crystals and in solution, have a light green color. The oxide is black; the salts slightly redden litmus. The sulphate (*7 ag.*) is efflorescent; the chloride, bromide, iodide, and citrate are deliquescent; the hydrate, chlorate, and sulphite are especially instable.

The *hydroxide*, *oxide*, *carbonate*, *sulphite*, *phosphate*, *borate*, *oxalate*,

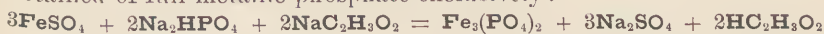
cyanide, ferrocyanide, *ferricyanide*, tartrate, and tannate are **insoluble** in water. In **analysis**, ferrous compounds are identified as ferrous by their blue precipitate with ferriecyanide (208); and, as iron, by the red solution which, after oxidation, they form with sulphocyanate.

**204. Reactions of Ferrous Salts.**—The **alkali hydrates** precipitate *ferrous hydroxide*,  $\text{Fe}(\text{OH})_2$ , white if pure, but seldom obtained sufficiently free from ferric hydrate to be clear white, and quickly changing, in the air, to ferroso-ferric hydroxide, of a dirty-green to black color, then to ferric hydroxide (212), of a reddish-brown color. The fixed alkalis adhere to this precipitate. **Ammonium chloride** or sulphate, sugar, and many organic acids, to a slight extent, dissolve the ferrous hydrate or prevent its formation (compare 154).

**205.** The soluble **carbonates** precipitate, from purely ferrous solutions, *ferrous carbonate*,  $\text{FeCO}_3$ , white if pure, but soon changing, in the air, to the reddish-brown ferric hydrate (212).

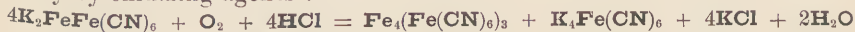
**206. Hydrosulphuric acid** does not disturb ferrous salts—the acetate being only slightly precipitated, as explained in 157. **Ammonium sulphide** precipitates *ferrous sulphide*,  $\text{FeS}$ , black. The moist precipitate is slowly converted, in the air, to ferrous sulphate; and afterward to basic ferric sulphate,  $\text{Fe}_2\text{O}(\text{SO}_4)_2$ .

**207. Alkali phosphates**—as  $\text{Na}_2\text{HPO}_4$ —precipitate two-thirds metallic *ferrous phosphate*,  $\text{FeHPO}_4$ , mixed with the full-metallic salt,  $\text{Fe}_3(\text{PO}_4)_2$ , white to bluish-white. By the addition of an alkali acetate, the precipitate is obtained of full-metallic phosphate exclusively:



**208. Cyanides**—as **KCN**—give a yellowish-red precipitate, chiefly ferrous cyanide, soluble in excess of the reagent; the solution constituting potassium ferrocyanide.

**Ferrocyanides**—as  $\text{K}_4\text{Fe}(\text{CN})_6$ —precipitate *potassium-ferrous ferrocyanide*,  $\text{K}_2\text{FeFe}(\text{CN})_6$  (Everitt's salt), bluish-white, insoluble in acids. This is converted to Prussian blue (217), gradually by exposure to the air, immediately by oxidizing agents:



**Ferricyanides**—as  $\text{K}_6\text{Fe}_2(\text{CN})_{12}$ —precipitate (even from dilute solutions) *ferrous ferricyanide*,  $\text{Fe}_3\text{Fe}_2(\text{CN})_{12}$ , dark blue, insoluble in acids. *This important test reveals the presence of traces of ferrous salt, in ferric solutions.* For this purpose the solution must be dilute, as stated at 217, and the *original solution* always employed, because the oxidation of iron is altered by chemical operations.

**Alkali hydroxides** decompose the precipitates above named: with potassium ferrous ferrocyanide, forming alkali ferrocyanide and ferrous hydroxide; with ferrous ferricyanide, forming alkali ferricyanide and ferrous hydroxide:



Sulphocyanates give no reaction with ferrous salts.

209. Oxalic acid and oxalates precipitate ferrous oxalate,  $\text{FeC}_2\text{O}_4$ , yellowish-white, crystalline, sparingly soluble in boiling water, decomposed by mineral acids not too dilute.

210. Tannic acid, and tincture of galls, with concentrated solutions of purely ferrous salts, give a white gelatinous precipitate of ferrous tannate, which is quickly oxidized by exposure to the air to blue-black ferric tannate—long used for writing ink.

211. By ignition and in beads before the oxidizing flame of the blow-pipe ferrous salts give the same reactions as ferric (220).

212. Solubilities of Ferric Salts.—FERRIC salts form solutions having a brownish yellow color, and reddening litmus. Most soluble ferric salts are deliquescent. Ferric oxide, in powder, is reddish-brown; in native crystal, steel-gray. It is soluble in hydrochloric acid, not very readily, but much quicker than in other acids.

The hydroxide, oxalate, phosphate, ferrocyanide, tannate, gallate, borate, and sulphite are insoluble in water. The chloride is soluble in alcohol and in ether; the sulphate is soluble in alcohol, a separation from ferrous sulphate. Ferric carbonate is not formed, and ferric sulphide is not formed in ordinary conditions of wet analysis. In analysis, ferric compounds are identified by the red solution they form with sulphocyanate, and distinguished from ferrous forms by not causing a blue precipitate with ferriicyanide (217). Ferricium is separated in the First Division of Group III., with the other pseudo-triads.

213. Reactions of Ferric Salts.—The alkali hydroxides precipitate ferric hydroxide,  $\text{Fe}_2(\text{OH})_6$ , variable to  $\text{Fe}_2\text{O}_2(\text{OH})_2$ , reddish-brown, insoluble in alkalis or ammonium salts. Salts of fixed alkalis adhere to this precipitate with great tenacity.

Alkali carbonates—as  $\text{K}_2\text{CO}_3$ —also precipitate the hydroxide, containing traces of carbonate. Regarding barium carbonate, see 219.



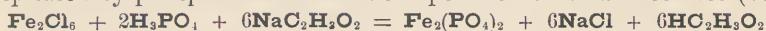
214. Hydrosulphuric acid does not precipitate iron from ferric solutions; but reduces them to the ferrous combination, with precipitation of sulphur.

215. Ammonium sulphide precipitates the ferrous sulphide with free sulphur,  $\text{FeS}$  with  $\text{S}$ , a reduction of the metal to the condition of a dyad. Hence, the ammonium sulphide precipitate contains iron in ferrous condition only.

216. Phosphates—as  $\text{Na}_2\text{HPO}_4$ —precipitate ferric phosphate,  $\text{Fe}_2(\text{PO}_4)_2$ , scarcely at all soluble in acetic acid, but readily soluble in hydrochloric,



nitric, and sulphuric acids. Hence, ferric salts which are not acetates are precipitated by phosphoric acid with co-operation of alkali acetates (207):



In this way phosphoric acid is removed from alkaline earth bases—in solutions of alkaline earth phosphates, in hydrochloric or nitric acid.

**217. Soluble cyanides**—as **KCN**—precipitate, from ferric salts, the *hydrate*, with evolution of hydrocyanic acid (*a*).

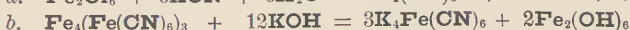
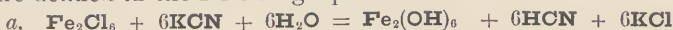
**Ferrocyanides**—as **K<sub>4</sub>Fe(CN)<sub>6</sub>**—precipitate *ferric ferrocyanide*, **Fe<sub>4</sub>(Fe(CN)<sub>6</sub>)<sub>3</sub>**, Prussian blue, insoluble in acids, decomposed by alkalis (*b*). Strong acids color the reagent blue, and render the test fallacious; acetic acid is free from this objection, and addition of potassium acetate enables the test to be made in acid solutions. By excess of the reagent the precipitate is somewhat soluble to a blue liquid.

**Sulphocyanates**—as **KCNS**—form, in solution, *ferric sulphocyanate*, **Fe<sub>2</sub>(CNS)<sub>6</sub>**, of a blood-red color so intense that this is an exceedingly delicate test for iron when in the ferric condition (*c*).

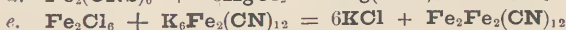
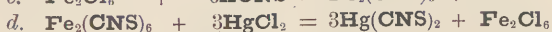
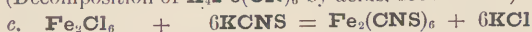
The red salt is freely soluble in water, alcohol, and ether, and extracted by ether from aqueous solutions; is decomposed by alkalis, but not by acids. Traces of ferric salts are revealed by adding the reagent, slightly over-saturating the mixture with **ether**; the excess of which will rise to the surface, colored by any ferric sulphocyanate, concentrated from the mixture.\* The color of the liquid is destroyed by mercuric chloride (*d*); also by phosphates, borates, acetates, oxalates, tartrates, racemates, malates, citrates, succinates, and the acids of these salts. Molybdenum dioxide, also nitric and chloric acids, give red color with the sulphocyanate, removed by heat. To determine the condition of iron *the original solution* only can be used (202).

**Ferricyanides**—as **K<sub>3</sub>Fe<sub>2</sub>(CN)<sub>12</sub>**—form *no precipitate* in ferric solutions, but give a green, or, in some proportions, brown color to the liquid (*e*), which should be *diluted* until transparent enough to reveal minute portions of blue precipitate if ferrous salt is present (208). The addition of *stannous chloride*, **SnCl<sub>2</sub>**, or some other strong deoxidizing agent to the mixture of ferricyanide, wherein no precipitate is found, constitutes a delicate test for ferric salts.

Some of the above-named reactions of ferric salts with cyanogen compounds are defined in the following equations:



(Decomposition of **K<sub>4</sub>Fe(CN)<sub>6</sub>** by acids, see Part II.)



**218. The acetates**—as **NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>**—form, in the cold, a dull red liquid, ferric acetate, **Fe<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>6</sub>**, not decolorized by mercuric chloride. On boil-

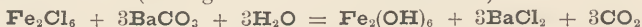
\* NATANSON, *Zeitsch. analyt. Chem.*, iii. 370.

ing the solution basic ferric acetate is precipitated, finally becoming hydrate. **Sulphites** give, likewise, a red solution of ferric sulphite, decomposed by boiling.\*

**219. Tannic acid**—and tincture of galls—precipitate ferric salts blue-black, as ferric tannate, the basis of common ink.

**Ammonium Succinate** precipitates reddish-brown ferric succinate.

**Carbonates of Ba, Ca, Mg, Mn, Zn, and Cu** precipitate ferric hydroxide from the chloride even in the cold (leaving barium chloride in solution) :



The excess of the barium carbonate is filtered out with the ferric hydroxide, and may be separated by addition of sulphuric acid, which changes it to insoluble barium sulphate, and leaves ferric sulphate in solution. If ferrous chloride were in the original solution, the barium chloride formed in the reaction may be separated from it, likewise, by addition of sulphuric acid.

**220.** The larger number of iron salts are decomposed, as solids, by **heat**; ferric chloride vaporizes, undecomposed, at a very little above  $100^\circ \text{C}$ . ( $212^\circ \text{F}$ .) **Ignition** in the air changes ferrous compounds, and ignition on charcoal or by the reducing flame changes ferric compounds to the *magnetic oxide*, which is attracted to the magnet.

In the outer **flame**, the **borax bead**, when moderately saturated with any compound of iron, acquires a reddish color while hot, fading and becoming light *yellow* when cold, or colorless, if feebly saturated. The same bead, held persistently in the *reducing* flame, becomes colorless unless strongly saturated, when it shows the pale *green* color of ferrous compounds. The reactions with **microcosmic salt** are less distinct, but similar. Cobalt, nickel, chromium, and copper conceal the reaction of iron in the bead.

Ferric compounds, heated briefly in a **blue borax bead** holding a very little **cupric oxide**, leave the bead blue; ferrous compounds so treated change the blue bead to red—the color of cuprous oxide.

## 221. Recapitulation of Distinctions between Ferric and Ferrous Compounds :

### *Ferric Compounds.*

### *Ferrous Compounds.*

- |                     |   |   |
|---------------------|---|---|
| (1) Ferricyanides.  | No pre., green color, 217.                          | Deep blue pre. $\text{Fe}_3\text{Fe}_2(\text{CN})_{12}$ . |
| (2) Sulphocyanates. | Red sol. $\text{Fe}_2(\text{CNS})_6$ .              | No change.  |
| (3) Ferrocyanides.  | Blue pre. $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ . | Pale blue pre. $\text{K}_2\text{FeFe}(\text{CN})_6$ .     |
| (4) Carbonates.     | Effervescence (213).                                | No effervescence (205).                                   |
| (5) Cyanides.       | 217.  | 208.  |

\* Meconic acid and Formic acid form red solutions *with ferric salts*. Benzoic acid gives a flesh-colored precipitate; salicylic acid a deep violet color; phenol and creosote, each a blue color; saligenin a blue color; and various compounds of the "aromatic group," hydroxyl substitutions in benzene derivatives, give blue to violet colors. Morphine, pseudomorphine, and daphnin give the blue color.

## (6) Reducing agents.

Hydrosulph. acid. (Deodorized and S.  
precipitated.)

Sulphurous acid. (Deodorized.)

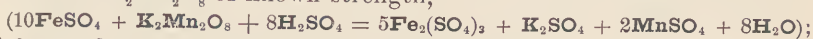
## (7) Oxidizing Agents.

Nitric acid, . . . . . 202 (e) (Brown gas, by heat.)

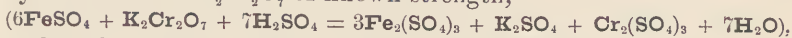
Bromine, . . . . . (Deodorized.)

Chlorine water, . . . . . (Deodorized.)

**222. Estimation of Fe''.**—(1) By conversion into  $\text{Fe}_2\text{O}_3$  and weighing as such ; (2) by converting it into  $\text{FeS}$  and weighing as such ; (3) by treating with  $\text{AuCl}_3$  and weighing the reduced gold ; (4) volumetrically (a) by a solution of  $\text{K}_2\text{Mn}_2\text{O}_8$  of known strength,

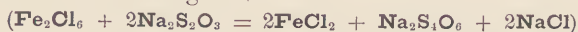


(b) by a solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  of known strength,



the end of the reaction is determined by  $\text{K}_6\text{Fe}_2(\text{NC})_{12}$ .

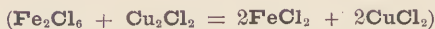
**223. Estimation of  $(\text{Fe}_2)^{\text{VI}}$ .**—(1) It is converted into  $\text{Fe}_2\text{O}_3$  or  $\text{FeS}$ , and weighed as such ; also (2) volumetrically (a) by a solution of sodium thiosulphate of known strength



A few drops of a solution of  $\text{CuSO}_4$  are added. The  $\text{CuSO}_4$  in some manner not well understood hastens the reaction and gives more accurate results. The end of the reaction is shown by  $\text{KCNS}$  ; (b) by a solution of  $\text{SnCl}_2$  of known strength



The excess of  $\text{SnCl}_2$  used is determined by a solution of iodine in  $\text{KI}$ , and deducted from the whole amount used ; (c) by a solution of  $\text{Cu}_2\text{Cl}_2$  of known strength



A drop of  $\text{KCNS}$  is first added, and the reduction is complete when the color disappears.

**224. Oxidation.**—Metallic iron precipitates the free metals from solutions of  $\text{Au}$ ,  $\text{Pt}$ ,  $\text{Ag}$ ,  $\text{Hg}$ ,  $\text{Bi}$ , and  $\text{Cu}$ .

Solutions of  $\text{Fe}'$  are changed to  $(\text{Fe}_2)^{\text{VI}}$  solutions by treating with solutions of  $\text{Au}'''$ ,  $\text{Ag}'$ ,  $\text{Cr}^{\text{VI}}$ ,  $\text{Mn}^{\text{VII}}$ ,  $\text{Mn}^{\text{VI}}$ , and  $\text{H}_2\text{O}_2$ . In presence of some dilute acid, such as  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$  by  $\text{PbO}_2$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{Ni}_2\text{O}_3$ . The following acids also oxidize  $\text{Fe}'$  to  $(\text{Fe}_2)^{\text{VI}}$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{HClO}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$ ,  $\text{H}_2\text{SO}_4$  (if concentrated and hot),  $\text{HBrO}$ ,  $\text{HBrO}_3$ ,  $\text{HIO}_3$ ,  $\text{Br}$ ,  $\text{Cl}$ .  $\text{Br}$  and  $\text{Cl}$  in presence of  $\text{KOH}$  changes  $\text{Fe}'$  and  $(\text{Fe}_2)^{\text{VI}}$  to  $\text{K}_2\text{FeO}_4$ .

**225.  $(\text{Fe}_2)^{\text{VI}}$**  is changed to  $\text{Fe}''$  by solutions of  $\text{Sn}''$ ,  $(\text{Cu}_2)''$ ,  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{SO}_2$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , and  $\text{HI}$ . Also by nascent hydrogen, or by



any of the metals which produce hydrogen when treated with acids, including Zn, Sn, Cd, Al, As, Sb, Bi, Pb, Cu, and Fe.

**MANGANESE.** Mn = 54.855.

**226. Specific gravity** 7.14 to 7.20 (BRUNNER). *Melts at the highest heat of the blast furnace* (CLARKE).

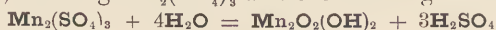
**227. Occurrence.**—Not found native. Its chief ore is pyrolusite ( $\text{MnO}_2$ ). It is also found as braunite ( $\text{Mn}_2\text{O}_3$ ), hausmannite ( $\text{Mn}_3\text{O}_4$ ), manganite ( $\text{Mn}_2\text{O}_2(\text{OH})_2$ ), manganese spar ( $\text{MnCO}_3$ ), manganese blende ( $\text{MnS}$ ), and as a constituent of many other minerals.

**228. Preparation.**—(1) By electrolysis of the chloride. (2) By reduction with metallic sodium. (3) By reduction with some form of carbon. It has not been reduced by hydrogen.

**229. Properties.**—A brittle metal, having the appearance of cast iron; harder than steel, and when mixed with it improves its quality. It oxidizes in the air, and must be kept under naphtha. It decomposes water at ordinary temperatures, rapidly when heated.

**230. Oxides and Hydroxides.**—Manganous oxide ( $\text{MnO}$ ) represents the only base capable of forming stable manganese salts. It is formed (1) by simple ignition of  $\text{Mn}(\text{OH})_2$ ,  $\text{MnCO}_3$ , or  $\text{MnC}_2\text{O}_4$ , air being excluded. (2) By ignition of any of the higher oxides of manganese with hydrogen in a closed tube. If prepared at as low a temperature as practicable, it is a dark gray or greenish gray powder and oxidizes quickly, in the air, to  $\text{Mn}_3\text{O}_4$ . If prepared at a higher heat it is more stable. Manganous hydroxide ( $\text{Mn}(\text{OH})_2$ ) is formed from manganous salts by precipitation with alkalis. It quickly oxidizes in the air, forming  $\text{Mn}_2\text{O}_2(\text{OH})_2$ , thus changing from white to brown.

**231. Manganic oxide** ( $\text{Mn}_2\text{O}_3$ ) is formed, (1) by heating  $\text{MnO}$ ,  $\text{Mn}_3\text{O}_4$ , or  $\text{MnO}_2$  to a red heat in oxygen gas (SCHNEIDER; *Pogg. Ann.* 107, 605); (2) by heating  $\text{Mn}(\text{OH})_2$ ,  $\text{Mn}(\text{NO}_3)_2$  or any of the higher or lower oxides in the air (FEHLING'S *Handbuch der Chemie*, 1886, 4, 253).  $\text{Mn}_2\text{O}_2(\text{OH})_2$  (dimanganic dioxide dihydroxide) is formed (1) by oxidation of  $\text{Mn}(\text{OH})_2$  in the air; (2) by treating  $\text{MnO}_2$  with concentrated  $\text{H}_2\text{SO}_4$  at a temperature of about  $130^\circ \text{C}$ ., forming  $\text{Mn}_2(\text{SO}_4)_3$  and then adding water,

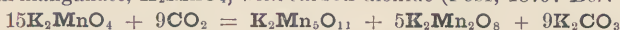


(CARIUS, 1856, *Ann. Ch. Pharm.* 98, 63).

**232. Trimanganese tetroxide** ( $\text{Mn}_3\text{O}_4$ ) is formed when any of the higher or lower oxides of manganese or any manganese salts with a volatile acid are heated in the air to a white heat. The corresponding hydroxide would be  $\text{Mn}_2(\text{OH})_3$ ; this has not been isolated. A corresponding oxide hydroxide is formed by adding freshly formed and moist  $\text{MnO}_2$  to an excess of  $\text{MnCl}_2$ , containing  $\text{NH}_4\text{Cl}$  (OTTO, 1855).

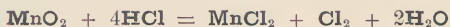
**233. Manganese peroxide** ( $\text{MnO}_2$ ) is formed (1) by heating  $\text{Mn}(\text{NO}_3)_2$  to  $200^\circ \text{C}$ . (KUHLMANN, 1874); (2) by heating  $\text{MnCO}_3$  with  $\text{KClO}_3$  to  $300^\circ \text{C}$ .; (3) by boiling any manganous salt with concentrated  $\text{HNO}_3$  and  $\text{KClO}_3$ . A corresponding hydroxide,  $\text{Mn}(\text{OH})_2$ , has not been isolated. Several oxide hydroxides—*e.g.*,  $\text{MnO}(\text{OH})_2$ ,  $\text{Mn}_2\text{O}_3(\text{OH})_2$ ,  $\text{Mn}_3\text{O}_4(\text{OH})_4$ , etc., have been produced.

**234. Manganites.**—The tetrad manganese ( $\text{Mn}^{\text{IV}}$ ) sometimes plays the part of an acid toward the stronger bases. Potassium manganite,  $\text{K}_2\text{Mn}_5\text{O}_{11}$ , is formed by treating potassium manganate,  $\text{K}_2\text{MnO}_4$ , with carbon dioxide (Post, 1879: *Ber.* 1459).



Calcium manganite, ( $\text{CaMn}_5\text{O}_{11}$ ), has been isolated.  $\text{K}_2\text{MnO}_4$  with  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ , or other strong non-reducing acids, forms  $\text{MnO}_2$ , or one of its hydroxides.

**235. Manganese Dioxide**,  $\text{Mn}^{\text{IV}}\text{O}_2$ , constitutes the commercial source of manganese and an important oxidizing agent, as Pyrolusite. Salts of this type are not formed, and the action of hydrochloric acid with heat slowly dissolves (reduces) the dioxide to manganous chloride, with evolution of chlorine:



Free chlorine, bromine, and iodine are obtained in accordance with this reaction (or some modification of it), and immense quantities of native manganese dioxide are required for the liberation of these elements in manufacturing operations. The production of chlorine is frequently effected by using sulphuric acid and common salt, instead of hydrochloric acid:



Oxygen also can be obtained from binoxide of manganese, by action of sulphuric acid:



Further, regarding  $\text{Mn}^{\text{IV}}$  as an oxidizing agent, see Part II.

**236. Manganates.**—Manganic acid,  $\text{H}_2\text{Mn}^{\text{VI}}\text{O}_4$ , is not known in a free state. The corresponding potassium salt,  $\text{K}_2\text{MnO}_4$ , is formed when any form of manganese is fused with  $\text{KOH}$  or  $\text{K}_2\text{CO}_3$  (1) in the air, see (b) and (c) (249), oxygen being absorbed; or (2) with  $\text{KNO}_3$  or  $\text{KClO}_3$ ,  $\text{NO}$  or  $\text{KCl}$  being formed. A manganate of the alkali metals is soluble in water, with gradual decomposition into manganese dioxide and permanganates:

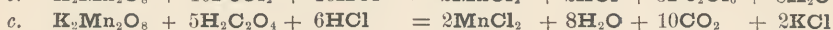
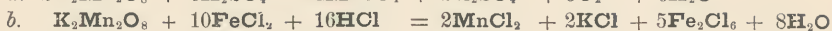


Free alkali retards, and free acids and boiling promote, this change. Manganates have a green color, which turns to the red of permanganates during the decomposition inevitable in solution. This is the usual method of manufacturing  $\text{K}_2\text{Mn}_2\text{O}_8$ .

**237. Permanganic Acid** is not in use as an acid, but is represented by the permanganates, as  $\text{K}_2(\text{Mn}_2)^{\text{XIV}}\text{O}_8$ .\* The permanganic acid radical is at once decomposed by addition of strong acids to a solid permanganate, but in water solution this decomposition does not at once take place, except by contact with oxidizable substances. The oxidizing power of permanganates extends to a great number of substances, possesses different characteristics in acid and in alkaline solutions, acts in many cases so rapidly as to be violently explosive, and is of such quantity that four parts of the absolute potassium salt furnish over one part of oxygen (equation a).

For the study of Permanganates in oxidation, see Part II. The reactions with **ferrous salts** (b) and with oxalic acid (c) are much used in volumetric analysis:

\* In permanganates, manganese may be considered as an octad, in the compounds of which two of its atoms are held to each other by one bond of each; the pair having twice seven bonds for other elements, and having always an even number of atoms in correctly written formulæ.



238. Permanganates are all **soluble** in water, silver permanganate being only sparingly soluble. The most of them are **deliquescent**. Their solutions have a deep red **color**. Slight deoxidation may give the green color of manganate.

239. Manganese is reduced to the manganous condition, from all its other degrees of combination, by boiling with hydrochloric acid. In this, its only stable form, it is most perfectly **identified as manganese**, and the various reactions of (a) the manganous base in the wet way obtained—240 and after.

b. For reactions characteristic of the **manganic base**, see 251 and after.

c. If the substance be a black powder, insoluble in water, but dissolving to manganous chloride in hydrochloric acid, with evolution of chlorine even in the cold (235), it is **MnO<sub>2</sub>**, **Mn<sub>2</sub>O<sub>3</sub>**, **Mn<sub>3</sub>O<sub>4</sub>**, or a mixture of these or their hydroxides.

d. If having a green color (236), and being soluble in water with decomposition, etc., leaving **MnO<sub>2</sub>**, it is a **manganate**, representing manganic acid.

e. If soluble in water to a red color, and, by deoxidation, losing color (and leaving manganous base or **MnO<sub>2</sub>**), it is indicated as a **permanganate** (237), representing permanganic acid.

240. **Solubilities of Manganous Salts.**—The chloride (4 *aq.*), bromide, iodide, and nitrate, are **deliquescent**; the sulphate (7 *aq.*) is efflorescent.

Manganous oxide, *hydroxide*, *sulphide*, *carbonate*, *phosphate*, *oxalate*, *borate*, and *sulphite*, are **insoluble** in water. The *hydroxide* is insoluble in alkalies, but soluble in solution of ammonium salts.

241.—**Reactions of Manganous Salts.**—In **analysis**, manganese is identified by the oxidation of manganous hydroxide or oxide, to manganate (248) or permanganate (248), each recognized by its bright color. As to determination of the oxidation of manganese, see 239

242. The **alkali hydrates** precipitate, from soluble manganous salts, *manganous hydroxide*, **Mn(OH)<sub>2</sub>**, white, soon turning brown in the air by oxidation to dimanganic dioxide dihydroxide, **Mn<sub>2</sub>O<sub>2</sub>(CH)<sub>2</sub>**.

The precipitate is insoluble in excess of alkali, but—before oxidation—is soluble in solution of **ammonium salts**, by formation of soluble double salts of ammonium and manganese—ammonio-manganous salts—(corresponding to those of ammonium and magnesium; compare 76). And hence, **ammonium hydroxide** precipitates but part of the manganese in solution, forming in the reaction a salt of ammonium, which holds the rest of the manganese from precipitation.

The *manganic hydroxide* is not only insoluble in ammonium salts, but it is formed and precipitated from the ammoniacal solution of manganous hydroxide in salts of ammonium by action of **the air**. After standing, all the manganese is so precipitated, dark brown; this precipitation by action of the air upon solution in ammonium salt being peculiar to manganese. As free ammonia facilitates the oxidation of metallic copper and of cobaltous salts, it may here promote the oxidation of the manganous compounds; also, it neutralizes the acid which would otherwise be set free.

**243. Hydrosulphuric acid** precipitates manganous acetate but imperfectly, and not in presence of acetic acid, and does not precipitate other salts, as manganous sulphide is soluble in very dilute acids, even acetic acid. **Ammonium sulphide** precipitates from neutral solutions, and forms from the recent hydrate of mixtures made alkaline the flesh-colored *manganous sulphide*,  $\text{MnS}$ . Acetic acid, acting on the precipitated sulphides, separates manganese from cobalt and nickel, and from the greater part of zinc.

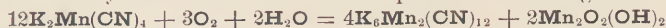
**244. Alkali carbonates** precipitate *manganous carbonate*,  $\text{MnCO}_3$ , white, oxidized by the atmosphere to the brown manganic hydroxide (242), and, before oxidation, somewhat soluble in solution of ammonium chloride.

**245. Alkali phosphates**—as  $\text{Na}_2\text{HPO}_4$ —precipitate, from neutral solutions of manganous salts, normal *manganous phosphate*,  $\text{Mn}_3(\text{PO}_4)_2$ , white, slightly soluble in water, and soluble in dilute acids. It turns brown in the air.

The manganous hydrogen phosphate— $\text{MnHPO}_4$ —is more soluble in water, and is obtained by crystallization from a mixture of manganous sulphate acidulated with acetic acid, and disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4$ , added till a precipitate begins to form. From the **ammonio-manganese solution** (242) phosphates precipitate all the manganese as *ammonium-manganous phosphate*.

**246. Alkaline oxalates** precipitate *manganous oxalate*, soluble in acids not very dilute, and formed with difficulty by addition of oxalic acid.

**247. Soluble cyanides**—as  $\text{KCN}$ —precipitate *manganous cyanide*,  $\text{Mn}(\text{CN})_2$ , white, but darkening in the air, soluble in excess of the precipitant by formation of *double cyanides*—as  $\text{K}_2\text{Mn}(\text{CN})_4$ . This solution, exposed to the air, produces *manganicyanides*—analogous to ferri-cyanides—with oxidation of a portion of the manganese :



**Ferrocyanides** precipitate white *manganous ferrocyanide*,  $\text{Mn}_2\text{Fe}(\text{CN})_6$ , soluble in hydrochloric acid. **Ferri-cyanides** precipitate brown *manganous ferri-cyanide*,  $\text{Mn}_3\text{-Fe}_2(\text{CN})_{12}$ , insoluble in acids.

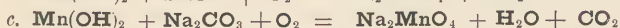
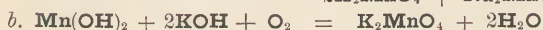
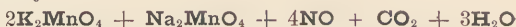
**248.** Manganese is most easily and certainly identified through **oxidation**, by several methods, each method giving a *color-product*.

A small portion of manganous solution, when boiled with **nitric acid** or **dilute sulphuric acid** and **lead dioxide**, or  $\text{Pb}_3\text{O}_4$ , is **oxidized** to *permanganic acid*,  $\text{H}_2\text{Mn}_2\text{O}_8$ , giving a red color to the solution when the sediment subsides. The oxidation is derived from the lead dioxide, reduced to a lead salt. If other reducing agents are present, they also must be oxidized. The lead dioxide should be used in such excess as to leave a black sediment. An excess of  $\text{MnO}_2$  must not be mistaken for an excess of  $\text{PbO}_2$ .

**249. Ignition with alkali and oxidizing agents**, forming a *bright green* mass of alkaline *manganate*, constitutes a delicate and convenient test for manganese, in any combination. A small portion of precipitate or fine powder is taken. If the manganese forms but a small part of a mixture to be



tested, it is better to submit the substance to the systematic course of analysis, and apply this test to the precipitate by alkali, in the third group. A convenient form of the test is by **ignition on platinum foil with potassium or sodium nitrate and sodium carbonate** (*a*). Ignition, by an **oxidizing flame**, on platinum foil, with potassium hydroxide, effects the same result, less quickly and perfectly (*b*). Ignition by the oxidizing flame of the blow-pipe, in a **bead of sodium carbonate**, on the loop of platinum wire, also gives the green color (*c*).



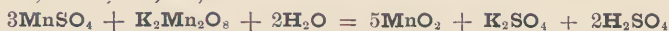
**250.** With beads of borax and microcosmic salt, before the outer blow-pipe flame, manganese colors the bead violet while hot, and *amethyst-red* when cold. The color is due to the formation of *manganic oxide*, the coloring material of the amethyst and other minerals, and is slowly destroyed by application of the inner flame, which reduces the manganic to manganous oxide.

**251. MANGANIC SALTS** are somewhat instable compounds, of a reddish-brown or purple red color, becoming paler and of lighter tint in reduction to the manganous combination. The chloride and sulphate are **deliquescent**. Manganic chloride,  $\text{Mn}_2\text{Cl}_6$ , exists only in solution, which is *reduced* to  $\text{MnCl}_2$  by boiling, also by evaporation to a solid. Manganic sulphate— $\text{Mn}_2(\text{SO}_4)_3$ —is soluble in dilute sulphuric acid, but is reduced to  $\text{MnSO}_4$  by the attempt to dissolve it in water alone, see 231; potassium manganic sulphate and other **manganic alums** are also decomposed by water.

**252. Hydrosulphuric acid** reduces manganic salts to the manganous combination, with precipitation of sulphur. **Ammonium sulphide** reduces manganic chloride, and precipitates *manganous sulphide*— $\text{MnS}$ —with free sulphur. **Alkali hydroxides, carbonates, and barium carbonate**, all precipitate from solution of manganic chloride, *manganic hydroxide*,  $\text{Mn}_2\text{O}_2(\text{OH})_2$ . **Ferrocyanides** precipitate gray-green *manganic ferrocyanide*,  $\text{Mn}_4(\text{Fe}(\text{CN})_6)_3$ . **Ferricyanides** precipitate *manganic ferricyanide*— $\text{Mn}_2\text{Fe}_2(\text{CN})_{12}$ —brown. When a manganic compound is mixed with aqueous **phosphoric acid**, the solution evaporated to dryness and gently ignited, a violet or deep blue mass is obtained, from which water dissolves a purple-red *manganic hydrogen phosphate*, a distinction from manganous compounds. Simple **ignition** changes manganic compounds to  $\text{Mn}_2\text{O}_4$ . In the tests in the **dry way**, manganic compounds give the same reactions as manganous oxide (249).

**253. Estimation.**—(1) By converting into  $\text{Mn}_3\text{O}_4$  (see 232), and weighing as such. (2) By precipitating as a sulphide and weighing after ignition in hydrogen. (3) By precipitating as  $\text{MnNH}_4\text{PO}_4$ , and after ignition weighing as  $\text{Mn}_2\text{P}_2\text{O}_7$ . (4) By addition of  $\text{K}_6\text{Fe}_2(\text{CN})_{12}$  in presence of **KOH** (and a trace of  $\text{Fe}_2(\text{OH})_6$ ), which converts the manganese into  $\text{MnO}_2$ , and the resulting  $\text{K}_4\text{Fe}(\text{CN})_6$  is estimated by  $\text{K}_2\text{Mn}_2\text{O}_8$ . (5) By treating the manganous salt with a solution of  $\text{K}_2\text{Mn}_2\text{O}_8$  of known strength. If some

$\text{ZnSO}_4$  is added the action is more satisfactory (WRIGHT and MENKE : *Jour. Chem. Soc.*, 1880, 37, 42).



254. *Peroxide* of manganese is estimated (1) by treating with  $\text{H}_2\text{C}_2\text{O}_4$ , and measuring or weighing the  $\text{CO}_2$  which is produced (246); (2) by boiling with  $\text{HCl}$  and estimating the evolved chlorine; (3) by boiling with  $\text{PbO}_2$  and  $\text{HNO}_3$ , and comparing the color with a permanganate solution of known strength (PETERS : *Chem. News*, 33, 35). A remarkable number of other methods have been recommended.

255. *Oxidation*.— $\text{Mn}''$  is oxidized to  $\text{Mn}^{\text{IV}}$  in alkaline mixture by  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{K}_6\text{Fe}_2(\text{CN})_{12}$ ,  $\text{KClO}$ ,  $\text{KBrO}$ , etc. In presence of  $\text{HNO}_3$  by  $\text{PbO}_2$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{HClO}_3$ ,  $\text{H}_2\text{Mn}_2\text{O}_8$ , etc.

256. All compounds of manganese having more than two bonds are reduced to  $\text{Mn}''$  by  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{H}_3\text{PO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HCNS}$ ,  $(\text{Hg}_2)''$ ,  $\text{Sn}''$ ,  $\text{As}'''$ ,  $\text{Sb}'''$  ( $\text{Cu}_2$ )'',  $\text{Fe}''$ ,  $\text{Cr}''$ , etc. For oxidizing action of  $\text{K}_2\text{MnO}_4$  and  $\text{K}_2\text{Mn}_2\text{O}_8$  see Part II.

COBALT.  $\text{Co} = 58.887$ .

257. *Specific gravity of powder reduced by hydrogen varies from 8.132 to 9.495; mean of five samples, 8.957* (RAMMELSBURG, 1849). *Melting point above that of gold and below that of iron* (CLARKE);  $1500^\circ \text{C}$ . ( $2732^\circ \text{F}$ .), PICTET, 1879.

258. *Occurrence*.—Cobalt does not occur in a free state, except in meteoric iron. It is found in linnæite ( $\text{Co}_3\text{S}_4$ ); skutterudite ( $\text{CoAs}_3$ ); speiss cobalt ( $\text{CoNiFeAs}_2$ ); glance cobalt ( $\text{CoFeAsS}_2$ ); wad ( $\text{CoMnO} \cdot 2\text{MnO}_2 + 4\text{H}_2\text{O}$ ), etc.

259. *Preparation*.—(1) By electrolysis of the chloride. (2) By heating with potassium or sodium (too expensive for commercial production). (3) By heating any of the oxides hydroxides or the chloride in hydrogen gas. (4) By fusion of the oxalate under powdered glass. (5) Also reduced by carbon in various ways.

260. *Properties*.—Cobalt in fine powder oxidizes rapidly in the air, and when made according to (3) sometimes takes fire spontaneously, like iron when reduced by hydrogen. When in a compact mass is permanent in dry air, and is only slightly tarnished in moist air. At a white heat it burns rapidly. Can be made magnetic, but, unlike steel, retains its magnetism at a white heat. It is harder than iron, malleable and ductile, cobalt wire being about twice as strong as iron wire. It is soluble in most dilute acids.

261. *Oxides and Hydroxides*.—Cobaltous oxide ( $\text{CoO}$ ) is made (1) by heating any of its oxides or hydroxides in hydrogen to (not above)  $350^\circ \text{C}$ .; (2) by ignition of  $\text{Co}(\text{OH})_2$  or  $\text{CoCO}_3$ , air being excluded; (3) by heating



$\text{Co}_3\text{O}_4$  to redness in a stream of  $\text{CO}_2$  (RUSSELL, 1863, *Jr. Chem. Soc.*, [2], 1, 51); (4) by heating any of the higher oxides to a white heat (C. D. BRAUN, 1867, *Zeit. Anal. Chem.*, 6, 76). Cobaltous hydroxide is made from cobaltous salts by precipitation with fixed alkalies; oxidizes if exposed to the air (264). The most stable oxide is the *cobaltoso-cobaltic* or *tri-cobaltic tetroxide* ( $\text{Co}_3\text{O}_4$ ); is made by heating any of the oxides or hydroxides, the carbonate, oxalate, or nitrate to a dull red heat in the air or in oxygen gas. Several oxide hydroxides are known—e.g.,  $\text{Co}_3\text{O}_2(\text{OH})_4$ ,  $\text{Co}_3\text{O}(\text{OH})_6$ ,  $\text{Co}_3\text{O}_3(\text{OH})_2$ . *Cobaltic oxide*,  $\text{Co}_2\text{O}_3$ , is made by heating the nitrate just hot enough for decomposition, but not hot enough to form  $\text{Co}_3\text{O}_4$ . Cobaltic hydroxide,  $\text{Co}_2(\text{OH})_6$ , is made by treating any cobaltous salt with  $\text{Cl}$ ,  $\text{HClO}$ ,  $\text{Br}$ , or  $\text{I}$  in presence of a fixed alkali or alkaline carbonate. It dissolves in  $\text{HCl}$ , with evolution of  $\text{Cl}$ , in  $\text{H}_2\text{SO}_4$ , with evolution of oxygen, forming a *cobaltous* salt.

**262. Solubilities.**—Cobaltous nitrate and acetate are **deliquescent**; chloride, hygroscopic; sulphate (7 *aq.*), efflorescent. The chloride **vaporizes**, undecomposed, at a high temperature.

The hydroxide, basic carbonate, sulphide, phosphate, borate, oxalate, cyanide, ferrocyanide, and ferricyanide are **insoluble** in water; the potassio-cobaltous oxide is insoluble; the ammonio-cobaltous oxide, soluble; the double cyanides of cobalt and the alkali metals are soluble in water. Alcohol dissolves the chloride and nitrate; ether dissolves the chloride, sparingly. Most of the salts insoluble in water form soluble compounds with ammonia. In **analysis**, cobalt is pretty clearly identified in the dry way, by the bead test (269).

**263. Reactions of Cobaltous Salts.**—Cobaltous oxide is gray-green, the hydroxide is rose-red; they are easily soluble in acids forming **COBALTOUS SALTS**, which exhibit bright colors, varied by different physical states, and by different chemical combinations. In crystals, they are red; anhydrous, mostly lilac. Their solutions are mostly blue when concentrated, but pink when diluted. At a certain stage of dilution, these solutions are red when cold, and blue when hot. The pink dilute solution of the chloride spreads colorless on white paper when cold, becomes blue on heating, and colorless when cold again, used as "*sympathetic ink*." Cobaltous oxide dissolves in melted glass, coloring it blue—used to cut off the light of yellow flames; also, with the same color, in fused borax—the most delicate test for cobalt (269), and in other vitreous substances. The black, cobaltoso-cobaltic oxide,  $\text{Co}_3\text{O}_4$ —as left by ignition of cobaltous oxide or nitrate—combines or mixes, by ignition, with zinc oxide from zinc compounds to form a green mass, with aluminium compounds to a blue, and with magnesium compounds to a pink mass. Cobalt forms many double salts, and compounds with alkalies, noted for their various bright colors.

**264.** The **fixed alkalies** precipitate, from solutions of cobaltous salts, blue *basic salts*, which absorb oxygen from the air and turn olive-green, as cobaltoso-cobaltic hydroxide; or if boiled before oxidation in the air, become rose-red, as *cobaltous hydroxide*,  $\text{Co}(\text{OH})_2$ . This last result is favored by excess of the reagent, which does not redissolve the precipitate. But ammonia and ammonium salts dissolve the precipitate.

**Ammonium hydrate** causes the same precipitate as **fixed alkalies**; incomplete, even at first, because of its solubility in the ammonium salt formed in the reaction, and soluble in excess of the ammonia to a solution which turns brown in the air by combination

with oxygen, and is not precipitated by potassium hydrate. The reaction of the precipitate with ammonium salts forms a soluble double chloride (as with magnesium); the reaction of the precipitate with ammonia produces, in different conditions, different soluble color compounds, ammonio-cobaltous and ammonio-cobaltic, as  $(\text{NH}_3)_4\text{CoCl}_2$ ,  $(\text{NH}_3)_6\text{CoCl}_2$ ,  $(\text{NH}_3)_5\text{Co}_2\text{Cl}_6$ , etc.

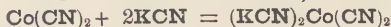
**265. Alkali carbonates** precipitate *cobaltous basic-carbonate*, peach red, which when boiled loses carbonic anhydride and acquires a violet, or, if the reagent be in excess, a blue color. The precipitate is soluble in ammonium carbonate (or in excess of that precipitant), and very slightly soluble in fixed alkali carbonates.

**Carbonates of Ba, Sr, Ca, and Mg** do not precipitate cobaltous salts in the cold (except the sulphate), but by prolonged boiling they precipitate cobaltous chloride completely.

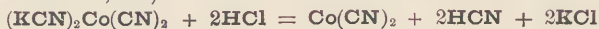
**266. Hydrosulphuric acid**, with normal cobaltous salts, gradually and imperfectly precipitates the black *cobalt sulphide*,  $\text{CoS}$ ; from cobalt acetate, the precipitation is more prompt, and is complete; but in presence of mineral acids, as in the second-group precipitation, no precipitate is made. When formed, the precipitate is scarcely at all soluble in dilute hydrochloric acid or in acetic acid; slowly soluble in moderately concentrated hydrochloric acid, as in dissolving the third-group precipitate; readily soluble in nitric, and most easily in nitro-hydrochloric acids. By exposure to the air, the recent cobaltous sulphide is gradually or slowly oxidized to cobalt sulphate, soluble, as occurs with iron sulphide. **Ammonium sulphide** precipitates immediately and perfectly the black  $\text{CoS}$ , described above.

**267. Phosphates**—as  $\text{Na}_2\text{HPO}_4$ —precipitate the reddish *cobaltous phosphate*,  $\text{CoHPO}_4$ , soluble in acids and in ammonia. Oxalic acid and **oxalates** precipitate the reddish white, *cobaltous oxalate*,  $\text{CoC}_2\text{O}_4$ , soluble in mineral acids and in ammonia.

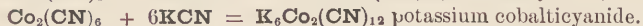
**268. Alkali cyanides**—as  $\text{KCN}$ —precipitate the brownish-white *cobaltous cyanide*,  $\text{Co}(\text{CN})_2$ , soluble in hydrochloric, not in acetic or in hydrocyanic acid, soluble in excess of the reagent, as double cyanides of cobalt and alkali metals— $(\text{KCN})_2\text{Co}(\text{CN})_2$ —potassium cobaltous cyanide, etc., the solution having a brown color:



Dilute **acids**, *without digestion*, reprecipitate cobaltous cyanide from this solution (the same as with nickel, 280):



But if the solution, with excess of the alkali cyanide and with a drop or two of hydrochloric acid, insuring free  $\text{HCN}$ , be now *digested* hot for some time, the cobaltous cyanide is oxidized and converted into alkali *cobalticyanide*—as  $\text{K}_6\text{Co}_2(\text{CN})_{12}$ —corresponding to ferricyanides, *but having no corresponding nickel compound*:



In the latter solution acids cause no precipitate (*important distinction from nickel*, whose solution remains  $(\text{KCN})_2\text{Ni}(\text{CN})_2$ , and after digestion as above is precipitated with acids).

**Sulphocyanate**, in highly concentrated solution, gives a *blue color*,  $\text{Co}(\text{CNS})_2$ , crystallizable in blue needles, soluble in alcohol, not in carbon disulphide. In less concentrated solutions, the color appears on warming. In neutral solutions, nickel, iron, manganese, and zinc do not interfere (SCHOENX, 1870).

**Ferrocyanides**—as  $\text{K}_4\text{Fe}(\text{CN})_6$ —precipitate *cobaltous ferrocyanide*,  $\text{Co}_2\text{Fe}(\text{CN})_6$ , gray-green, insoluble in acids. **Ferricyanides**—as  $\text{K}_3\text{Fe}_2(\text{CN})_{12}$ —precipitate *cobaltous ferricyanide*,  $\text{Co}_3\text{Fe}_2(\text{CN})_{12}$ , brownish-red, insoluble in acids. But a more distinctive

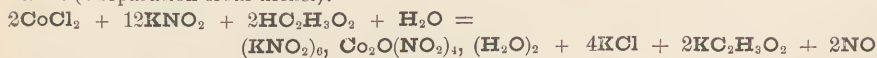
test is made by adding **ammonium chloride** and **hydroxide**, with the ferricyanide, when a *blood-red color* is obtained, in evidence of cobalt. If, in this test, manganese be present, a white precipitate is obtained at once, becoming brown with more ferricyanide; if nickel be present, a copper-red precipitate forms on boiling; zinc gives no precipitate, hot or cold, but on addition of ferrocyanide to the same solution, gives a white precipitate (ALLEN, 1871).

**269. In the bead of borax**, and in that of microcosmic salt, with oxidizing and with reducing flames, cobalt gives an intense *blue color*. The blue bead of copper changes to brown in the reducing flame. If strongly saturated, the bead may appear black from intensity of color, but will give a blue powder. This important test is most delicate with the borax bead. If sulphur or arsenic is present, it must be previously expelled by roasting. If manganese, copper, nickel, or iron is present, the continued application of the *reducing flame* will destroy the interfering color, and bring out the blue of cobalt.

By **ignition**, with sodium carbonate on charcoal or with the reducing flame, compounds of cobalt are reduced to a *magnetic mass*.

**270.** Cobaltous compounds are **oxidized to cobaltic** combinations, in the following tests, all of which distinguish cobalt from nickel, which is scarcely capable of higher oxidation.

**Potassium nitrite**,  $\text{KNO}_2$ , added to a somewhat concentrated solution of cobaltous salt, with addition of sufficient acetic acid, after warm digestion, on standing some time, better for twenty-four hours, causes a yellow crystalline precipitate of *potassium cobaltic nitrite* (a separation from nickel):



**Chlorine gas**, passed into dilute cobaltous solutions, changes them to cobaltic combinations, which are then precipitated by digestion with **barium carbonate** in the cold (compare 265). **Lead dioxide**, with warm digestion, precipitates from neutral solutions all the cobalt, as *cobaltic oxide hydroxide*.  $\text{Zn}(\text{OH})_2$ ,  $\text{Pb}(\text{OH})_2$ , and  $\text{HgO}$  precipitate  $\text{Co}(\text{OH})_2$  from  $\text{CoCl}_2$  at  $100^\circ \text{C}$ .

**271. Estimation.**—(1) As metallic cobalt, all compounds that may be reduced by ignition in hydrogen gas—*e.g.*,  $\text{CoCl}_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{CoCO}_3$ , and all oxides and hydroxides. (2) As  $\text{CoO}$ , all soluble cobalt salts, all salts whose acids are expelled or destroyed by ignition, all oxides and hydroxides. The salt is converted into  $\text{Co}(\text{OH})_2$  by precipitation with a fixed alkali, and ignited in a stream of  $\text{CO}_2$ . The carbonate and nitrate may be ignited directly in  $\text{CO}_2$ , and organic salts are first ignited in the air until the carbon is oxidized, and then again ignited in  $\text{CO}_2$ . (3) After converting into a sulphate it is ignited at a dull red heat and weighed as a sulphate. (4) After converting into the oxalate titrating with  $\text{K}_2\text{Mn}_2\text{O}_8$ .

**272. Oxidation.**— $\text{Co}''$  is oxidized to  $(\text{Co}_2)^\text{VI}$  in presence of a fixed alkali by  $\text{PbO}_2$ ,  $\text{Cl}$ ,  $\text{KClO}$ ,  $\text{Br}$ ,  $\text{KBrO}$ , and  $\text{I}$ ; in presence of acetic acid by  $\text{KNO}_2$  (270).  $(\text{Co}_2)^\text{VI}$  is reduced to  $\text{Co}''$  by  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{H}_3\text{PO}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HI}$ .

Metallic cobalt is precipitated from solution of  $\text{CoCl}_2$  by  $\text{Zn}$ ,  $\text{Cd}$ , and **Mg**.

NICKEL. Ni = 57.928.

**273. Specific gravity, reduced by carbon, 8.900** (SCHRÖDER, 1859). *Melting point, 1450° C. (2642° F.)* (PICTET, 1879).

**274. Occurrence.**—Nickel almost always occurs in nature together with cobalt. It is found as kupfernickel, **NiAs**, millerite or nickel blende, **NiS**, etc.

**275. Preparation.**—(1) By electrolysis. (2) By heating in a stream of hydrogen. The oxide is reduced in this manner at 270° C. (W. MÜLLER, 1869 : *Ann. Chim. Phys.*, **136**, 51). (3) By fusing the oxalate under powdered glass (**CO<sub>2</sub>** being given off). (4) Reduction by igniting in **CO**. (5) Reduction by fusing with carbon in a variety of methods.

**276. Properties.**—A hard white metal; malleable and ductile, making a stronger wire than iron; does not oxidize in the air at ordinary temperatures. It is much used in plating other metals. It is magnetic, but loses its magnetism like steel by heating to redness. Soluble in dilute **HCl** and **H<sub>2</sub>SO<sub>4</sub>**, hydrogen being given off; in concentrated **H<sub>2</sub>SO<sub>4</sub>**, **SO<sub>2</sub>** being formed; in **HNO<sub>3</sub>**, **NO** being evolved; in concentrated **HNO<sub>3</sub>** it becomes passive like iron.

**277. Oxides and Hydroxides.**—Nickelous oxide is formed when the carbonate, nitrate, or any of its oxides or hydroxides is strongly ignited. Nickelous hydroxide is formed by precipitation of nickelous salts with fixed alkalis. *Nickelic oxide*, **Ni<sub>2</sub>O<sub>3</sub>**, is made from **NiCO<sub>3</sub>**, **Ni(NO<sub>3</sub>)<sub>2</sub>**, or **NiO** by heating in the air not quite to redness, with constant stirring. It is changed to **NiO** at a red heat. *Nickelic hydroxide*, **Ni<sub>2</sub>(OH)<sub>6</sub>**, is formed by treating nickelous salts first with a fixed alkali and then with **Cl**, **NaClO**, **Br**, or **NaBrO** (not formed by iodine). A black powder, forming no corresponding salts. Soluble in **HCl**, **HBr**, and **HI**, with separation of **Cl**, **Br**, and **I**. Soluble in **HNO<sub>3</sub>**, **H<sub>2</sub>SO<sub>4</sub>**, and in most non-reducing acids with evolution of oxygen; in **H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>**, **CO<sub>2</sub>** being evolved, and in each case a *nickelous* salt being produced. A trinickelic tetroxide, **Ni<sub>3</sub>O<sub>4</sub>** (corresponding to **Co<sub>3</sub>O<sub>4</sub>**, **Fe<sub>3</sub>O<sub>4</sub>**, **Mn<sub>3</sub>O<sub>4</sub>**, and **Pb<sub>3</sub>O<sub>4</sub>**), is formed, according to A. BAUBIGNY (1878, *Compt. Rend.*, **87**, 1082), by heating **NiCl<sub>2</sub>** in oxygen gas at from 350° to 440° C.

**278. Solubilities.**—The salts of nickel have a delicate green color in crystals and in solution; when anhydrous, they are yellow. The nitrate and chloride are **deliquescent** or **efflorescent**, according to the hygrometric state of the atmosphere; the acetate is efflorescent. The chloride **vaporizes** at high temperatures.

The hydroxide, carbonate, sulphide, phosphate, borate, oxalate, cyanide, ferrocyanide, ferriecyanide, **insoluble** in water. The compounds of the oxide with potassium oxide and sodium oxide are insoluble; that with ammonia is soluble; and the double cyanides of nickel and alkali metals are soluble in water. The chloride is soluble in alcohol, and the nitrate in dilute alcohol. Most salts of nickel form soluble compounds by action of ammonium hydrate. In **analysis** nickel is separated, with cobalt, by the sparing solu-



bility of the sulphide in dilute acids. Its separation from cobalt is more difficult (280). In absence of cobalt, it is easily identified in the bead (282).

**279. Reactions of Nickelous Salts.**—The fixed alkali hydroxides precipitate nickelous hydroxide ( $\text{Ni}(\text{OH})_2$ ), pale green, insoluble in excess of the reagent and not oxidizable in the air, but soluble in ammonium hydroxide or ammonium salts to a greenish blue liquid (153).

**Ammonium hydroxide**, also, precipitates nickel hydroxide, soluble in excess, and in ammonium salts, with formation of compounds similar to those of cobalt (264), giving a violet-blue color to the solution. Sufficient potassium or sodium hydroxide will slowly reprecipitate nickel hydroxide from its ammoniacal solution, a distinction from cobalt. In dilute ammoniacal solutions, the blue color appears only after exposure to the air.

The alkaline **carbonates** precipitate basic carbonate of variable composition, green color, and soluble in ammonium carbonate, or excess of that precipitant—with blue or greenish-blue color. Carbonates of **Ba**, **Sr**, **Ca**, and **Mg** precipitate on boiling the whole of the nickel from  $\text{NiCl}_2$ .

With **hydrosulphuric acid**, and with **sulphide of ammonium**, nickel has the same deportment as cobalt (266): the precipitate being *nickel sulphide*, slightly soluble in excess of ammonium sulphide. **Phosphates**—as  $\text{Na}_2\text{HPO}_4$ —throw down *nickel phosphate*, greenish-white, mostly full metallic.

**280. Alkali cyanides**—as **KCN**—precipitate *nickel cyanide*,  $\text{Ni}(\text{CN})_2$ , yellowish-green, insoluble in hydrocyanic acid, and in cold dilute hydrochloric acid; dissolving in excess of the cyanide, by formation of soluble double cyanides—as potassium nickel cyanide ( $\text{KCN})_2\text{Ni}(\text{CN})_2$ . The equation of the change corresponds exactly to that for *cobalt* (263); and the solution of double cyanide is reprecipitated as  $\text{Ni}(\text{CN})_2$  by a careful addition of **acids** (like cobalt); but hot digestion, with the liberated hydrocyanic acid, forms no compound corresponding to cobaltcyanides, and does not prevent precipitation by acids (unlike cobalt). It will be observed that excess of hydrochloric or sulphuric acid will dissolve the precipitate of  $\text{Ni}(\text{CN})_2$ . **Ferrocyanides**—as  $\text{K}_4\text{Fe}(\text{CN})_6$ —precipitate a greenish-white *nickel ferrocyanide*,  $\text{Ni}_2\text{Fe}(\text{CN})_6$ , insoluble in acids, soluble in ammonium hydroxide, decomposed by fixed alkalies. **Ferricyanides** precipitate greenish-yellow *nickel ferricyanide*.

For the test by ferricyanide, with ammonium chloride and hydroxide, in distinction from *cobalt*, see 268.

Oxalic acid and **oxalates** precipitate, very slowly, but almost completely, after twenty-four hours, *nickel oxalate*, green.

**281. Chlorine**, or hypochlorite, in neutral solution, or, better, with fixed alkali hydroxide, forms a black precipitate of *nickelic hydroxide*,  $\text{Ni}_2(\text{OH})_6$ , reduced by heat or by solution in acids or in ammonium hydroxide. The separation of nickel from cobalt (270), by this test, is more accurate if potassium cyanide in excess be added previously to the chlorine or hypochlorite. Nitrites, with acetic acid, do not oxidize nickel as they do cobalt.

**282.** Nickel compounds dissolve clear in the **borax bead**, giving with the oxidizing flame a purple-red or violet color while hot, becoming yellowish-brown when cold; with the reducing flame, fading to a turbid gray, from reduced metallic nickel, and finally becoming colorless. The addition of any potassium salt, as potassium nitrate, causes the borax bead to take a dark purple or blue color, clearest in the oxidizing flame. With **microcosmic salt**, nickel gives a reddish-brown bead, cooling to a pale reddish-yellow, the colors being alike in both flames. Hence, with this reagent, in the reducing flame, the color of nickel may be recognized in presence of *iron* and *manganese*, which are colorless in the reducing flame; but *cobalt* effectually obscures the bead-test for nickel. The



yellow-red of *copper* in the reducing flame, persisting in beads of microcosmic salt, also masks the bead-test for nickel.

By **ignition** with soda on charcoal, compounds of nickel are reduced to a powder attracted by the *magnet*.

**283. Estimation.**—In gravimetric determinations nickel is converted into  $\text{NiO}$ , and after intense ignition weighed as such.

**284. Oxidation.**— $\text{Ni}''$  is changed to  $(\text{Ni}_2)^\text{vi}$  in presence of fixed alkalis by  $\text{Cl}$ ,  $\text{NaClO}$ ,  $\text{Br}$ , and  $\text{NaBrO}$  (not by  $\text{I}$ ).  $(\text{Ni}_2)^\text{vi}$  is reduced to  $\text{Ni}''$  by all non-reducing acids with evolution of oxygen; by reducing acids,  $\text{H}_2\text{C}_2\text{O}_4$  is oxidized to  $\text{CO}_2$ ,  $\text{HNO}_2$  to  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_2$  to  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{S}$  to  $\text{S}$ ,  $\text{H}_2\text{SO}_3$  to  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  to  $\text{Cl}$ ,  $\text{HBr}$  to  $\text{Br}$ ,  $\text{HI}$  to  $\text{I}$ ,  $\text{HCyS}$  to  $\text{HCy}$  and  $\text{H}_2\text{SO}_4$ ,  $\text{H}_4\text{Fe}(\text{CN})_6$  to  $\text{H}_6\text{Fe}_2(\text{CN})_{12}$ .

A solution of  $\text{NiCl}_2$  is reduced to the metallic state by zinc-dust and by finely divided cadmium or tin.

**ZINC.**  $\text{Zn} = 64.9045$ .

**285. Specific gravity**, 7.14 (RAMMELSBURG, 1880). *Melting point*,  $450^\circ \text{C}$ . ( $842^\circ \text{F}$ .) (PICTET, 1879). *Boiling point*,  $930^\circ \text{C}$ . ( $1706^\circ \text{F}$ .) (VIOLE, 1882).

**286. Occurrence.**—It is found as calamine ( $\text{ZnCO}_3$ ), as zinc-blende ( $\text{ZnS}$ ); also associated with other metals in numerous ores.

**287. Preparation.**—The process usually employed consists of two operations: (1) Roasting: in case of the carbonate the action is  $\text{ZnCO}_3 = \text{ZnO} + \text{CO}_2$ ; if it is a sulphide,  $2\text{ZnS} + 3\text{O}_2 = 2\text{ZnO} + 2\text{SO}_2$ . (2) Reduction with distillation; after mixing the  $\text{ZnO}$  with one-half its weight of powdered coal it is distilled at a white heat. Its usual impurities are **As**, **Cd**, **Pb**, **Cu**, **Fe**, and **Sn**. It is purified by repeated distillation, each time rejecting the first portion, which contains the more volatile **As** and **Cd**, and the last, which contains the less volatile **Pb**, **Cu**, **Fe**, and **Sn**. Strictly chemically pure zinc is best prepared from the carbonate which has been purified by precipitation.

Other methods of preparing zinc not financially profitable are: (1) Electrolysis; (2) reduction by **K**, **Na**, or **Mg**; (3) reduction by hydrogen; (4) reduction by carbon monoxide.

**288. Properties**—A bluish-white metal; retains its lustre in dry air, and is only slightly tarnished in moist air or in water. It is more malleable between  $100^\circ$  and  $150^\circ \text{C}$ . than at other temperatures, and may then be drawn into wire or rolled into sheets. At  $205^\circ \text{C}$ . it is so brittle that it may be easily powdered in a mortar.

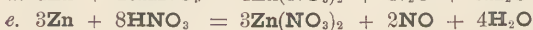
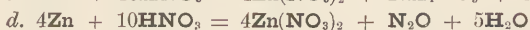
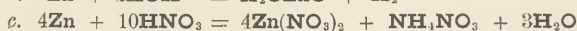
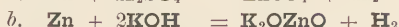
For use in the laboratory it is usually granulated by pouring it when melted into cold water. The water is then poured off and the zinc thrown into a solution containing about one grain of platinic chloride to a gallon of

water. Metallic platinum is precipitated upon the zinc ( $2\text{Zn} + \text{PtCl}_4 = \text{Pt} + 2\text{ZnCl}_2$ ), and increases its solubility in  $\text{H}_2\text{SO}_4$ . Otherwise (that is, if strictly chemically pure), it would be unfit for use in Marsh's test for arsenic.

**289. Oxide and Hydroxide.**—Zinc oxide ( $\text{ZnO}$ ) is made by igniting in the air either metallic zinc, its hydroxide, carbonate, nitrate, oxalate, or any of its organic oxysalts. Zinc hydroxide,  $\text{Zn}(\text{OH})_2$ , is made from solutions of zinc salts by precipitation with fixed alkalies (292).

**290. Solubilities.**—*Pure zinc* dissolves very slowly in acids or alkalies, unless in contact with copper, platinum, or some less positive metal. The metallic impurities in ordinary zinc enable it to dissolve easily with acids or alkali hydroxides. In contact with iron, it is quite rapidly oxidized in water containing air, but not dissolved by water, unless by aid of certain salts. All the agents which dissolve the metal, dissolve also its oxide and hydroxides.

The metal dissolves in hydrochloric, sulphuric, and acetic acids (*a*), and in the aqueous alkalies (*b*)—with evolution of hydrogen; in very dilute nitric acid, without evolution of gas (*c*); in moderately dilute cold nitric acid, mostly with evolution of nitrous oxide (*d*); and, in somewhat less dilute nitric acid, chiefly with evolution of nitric oxide (*e*). Concentrated nitric acid dissolves zinc but slightly—the nitrate being very sparingly soluble in nitric acid:

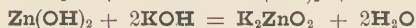
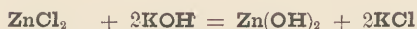


**291.** The *chloride*, bromide, iodide, chlorate, nitrate (6 *aq.*), and *acetate* (7 *aq.*) are **deliquescent**; the *sulphate* (7 *aq.*) is **efflorescent**.

The oxide, *hydroxide*, *sulphide*, *basic carbonate*, phosphate, arseniate, oxalate, and ferrocyanide are **insoluble** in water; the sulphite is sparingly soluble. Most salts of zinc, insoluble in water, form soluble compounds by action of any of the alkali hydroxides.

Zinc is **separated** from the metals of the third group, except from aluminium, by non-precipitation with excess of fixed alkali hydroxide in boiling solution; from aluminium, by precipitation as sulphide in alkali solution, and by non-precipitation with excess of ammonium hydroxide (292).

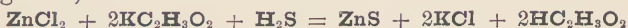
**292. Reactions of Zinc Salts.**—The alkali hydroxides all precipitate zinc hydroxide,  $\text{Zn}(\text{OH})_2$ , white, soluble in excess of either precipitant, with formation of potassium or sodium zinc oxide, or zincate,  $\text{K}_2\text{ZnO}_2$ , or  $\text{Zn}(\text{OK})_2$ :



All zinc salts are soluble in  $\text{KOH}$  and  $\text{Na}(\text{OH})$  except  $\text{ZnS}$ , and all in  $\text{NH}_4\text{OH}$  except  $\text{ZnS}$  and  $\text{Zn}_2\text{Fe}(\text{CN})_6$ .

On *boiling* the alkaline solutions, if dilute, a precipitate of zinc oxide separates, more readily from the ammoniac than from potassic or sodic solutions. In the *presence of iron*, or manganese, the zinc hydroxide does not so readily dissolve in the alkali precipitant, which in these cases needs to be very strong, at the time of precipitation.\* Hydroxide of zinc is somewhat soluble in ammonium chloride, as stated in 154.

**293. Hydrosulphuric acid** precipitates a *part* of the zinc from neutral solutions of its salts with mineral acids, and the whole from the acetate; also from other salts of zinc, if with addition of alkali acetates (separation from manganese):



That is: Zinc sulphide is not soluble in moderately dilute acetic acid, though much more soluble in mineral acids. The precipitate is *white* when pure.

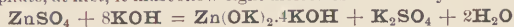
**294. Alkali sulphides**—as  $(\text{NH}_4)_2\text{S}$ —completely precipitate zinc as *sulphide*, both from its salts with acids and from its soluble combinations with alkalies.

**295. Alkali carbonates**—as  $\text{K}_2\text{CO}_3$ —precipitate *basic carbonate*, white,  $\text{Zn}_6(\text{OH})_6(\text{CO}_3)_2$ , sparingly soluble in ammonium carbonate, readily in ammonium hydrate. Carbonates of **Ba**, **Sr**, **Ca**, and **Mg** have no action at ordinary temperatures, but upon boiling precipitate the whole of the zinc.

**296. Alkaline cyanides**—as  $\text{KCN}$ —precipitate *zinc cyanide*,  $\text{Zn}(\text{CN})_2$ , white, soluble in excess of the precipitant. Alkaline *ferrocyanides*—as  $\text{K}_4\text{Fe}(\text{CN})_6$ —precipitate zinc ferrocyanide,  $\text{Zn}_2\text{Fe}(\text{CN})_6$ , white. Alkaline *ferricyanides*—as  $\text{K}_6\text{Fe}_2(\text{CN})_{12}$ —precipitate zinc ferricyanide,  $\text{Zn}_3\text{Fe}_2(\text{CN})_{12}$ , yellowish.

**297.** With sodium carbonate, on charcoal, before the *blow-pipe*, compounds of zinc are reduced to the metallic state. The metal is vaporized,

\* The solution of the zinc hydroxide precipitate, by addition of excess of alkalies, is greatly affected by conditions of temperature and dilution. At  $16^\circ$  to  $17^\circ$  C., one c.c. of Normal standard solution of zinc sulphate requires, to redissolve the precipitate, eight c.c. of Normal standard solution of potassium hydroxide. But now, just one-half of the alkali can be taken up, by adding four c.c. of half-Normal solution of sulphuric acid, before the precipitate reappears. That is, four molecules of the alkali hydroxide form and dissolve (or hold in a solution already made) the precipitate of one molecule of the zinc salt—supporting the equations in the text. But, if the equation is to represent the proportion of alkali necessary to add in order to make and dissolve the precipitate, at first, it must show eight molecules of alkali hydroxide to one zinc salt, thus:



The addition of water, at a certain point, precipitates the alkali solution after it is made. Heat does the same, as stated in the text. At  $50^\circ$  C., about three times as much of the alkali solution is required to dissolve the precipitate as at  $17^\circ$  C. The addition of an alkali solution so dilute as the tenth-Normal, in case of potassium hydroxide, does not effect full solution of the precipitate, however much is added. Sodium hydroxide solution is not required in quite so large excess to redissolve the precipitate—seven molecules being needed, in Normal solutions, instead of eight, as for potassium hydroxide. But the same proportion of four molecules is needed to hold the solution, after taking up excess by adding acid. In the case of ammonium hydroxide, 6.6 c.c. of Normal standard solution were found to be required to form and dissolve the precipitate from 1 c.c. of Normal solution of zinc salt. Then 1.6 c.c. of the alkali could be taken up by acid, before reprecipitation. Apparently, then, five molecules of ammonium hydroxide are required for soluble combination with one molecule of zinc salt. [See a report on Zinc and Alkali solutions, by the author and F. L. Wilson, *Jour. Amer. Chem. Soc.*, Feb., 1880, ii. 29.]

and then oxidized in the air, and deposited as a non-volatile coating, *yellow when hot and white when cold* (compare 160). If this coating, or zinc oxide otherwise prepared, be moistened with solution of **cobalt nitrate** and again ignited, it assumes a *green* color.

With borax or microcosmic salt, zinc compounds give a **bead** which, if strongly saturated, is yellowish when hot, and opaque white when cold.

**298. Estimation.**—Zinc is weighed (1) As an oxide, into which form it is brought by simple ignition if combined with a volatile inorganic oxyacid, otherwise it should be changed to a carbonate and then ignited. (2) It is converted into a sulphide, and after adding powdered sulphur it is ignited in a stream of hydrogen or hydrogen sulphide, and weighed as a sulphide. (3) It may be converted into  $\text{ZnNH}_4\text{PO}_4$ , and, after drying at  $100^\circ \text{C}$ ., weighed. Ignition converts it into  $\text{Zn}_3\text{P}_2\text{O}_7$ , with slight loss of zinc (CROOKES, 1886). (4) Volumetrically by converting it into the oxalate and titrating with potassium permanganate (W. G. LEISON). (5) Volumetrically by converting into  $\text{Zn}_2\text{Fe}(\text{CN})_6$  and titrating with potassium permanganate (M. RENARD).

**299. Oxidation.**—Metallic zinc precipitates the free metals from solutions of **Cd, Sn, Pb, Cu, Bi, Hg, Ag, Pt, Au, As, Sb, Te, In, Fe, Co, Ni, Pd, Rh, Ir, and Os** (*Gmelinkraut's Handbuch*, 3, 6). Solutions of  $\text{Cr}^{\text{VI}}$  are reduced to  $(\text{Cr}_2)^{\text{VI}}$ ; and compounds of manganese having more than two bonds are reduced to the dyad when acidulated with some non-reducing acid.

## 300. Comparison of some Reactions of Third-Group Bases.

*In Water Solution, as Chlorides, Nitrates, Sulphates, etc.*

	Aluminium.	Chromium.* (Cr <sub>3</sub> ) <sup>VI</sup>	Ferric. (Fe <sub>3</sub> ) <sup>VI</sup>	Ferrous. Fe <sup>II</sup>	Manganese. Mn <sup>II</sup>	Cobalt. (Cr) <sub>2</sub> <sup>VI</sup>	Nickel. Ni <sup>II</sup>	Zinc.
KOH or NaOH	Al <sub>2</sub> (OH) <sub>6</sub> <sup>+</sup>	Cr <sub>2</sub> (OH) <sub>6</sub> <sup>+</sup>	Fe <sub>3</sub> (OH) <sub>6</sub>	Fe(OH) <sub>2</sub>	Mn(OH) <sub>2</sub>	Co(OH) <sub>2</sub>	Ni(OH) <sub>2</sub>	Zn(OH) <sub>2</sub> <sup>†</sup>
NH <sub>4</sub> OH	"	"	"	"	"	"	"	"
NH <sub>4</sub> OH with NH <sub>4</sub> Cl	"	"	"	No pre.	No pre.	No pre.	No pre.	No pre.
Carbonates.	"	"	"	FeCO <sub>3</sub>	MnCO <sub>3</sub>	Basic Carb.	Basic Carb.	Basic Carb.
Sulphides.	"	"	FeS with S	FeS	MnS	CoS	NiS	ZnS
H <sub>2</sub> S in acid. sol.	No pre.	No pre.	S <sup>**</sup>	No pre.	No pre. <sup>***</sup>	††	††	††
Na <sub>2</sub> HPO <sub>4</sub>	Al <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>††</sup>	Cr <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>††</sup>	Fe <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> <sup>††</sup>	FeHPO <sub>4</sub> <sup>(207)</sup>	Mn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	CoHPO <sub>4</sub>	NiHPO <sub>4</sub>	ZnHPO <sub>4</sub>
Certain oxidizing agents.		Base to acid.		To ferric.	Base to acid.	Cobaltic acid.		
Certain reducing agents.		Acid to base.	To ferrous.		Acid to base.			

\* Chromic acid and its salts furnish (Cr<sub>2</sub>)<sup>VI</sup> as a base when treated with ammonium sulphide, hydrogen sulphide, and other reducing agents (194 a and d). The occurrence of Cr<sup>VI</sup> in the second and third groups should always be prevented by previous reduction to (Cr<sub>2</sub>)<sup>VI</sup>. A suitable method is to boil with hydrochloric acid (or with HCl and a few drops of alcohol) until the solution turns completely green.

† The precipitates soluble in excess of the reagent (167, 292).

†† The precipitates soluble in excess of the cold reagent, but thrown down again on boiling (181).

\*\* The precipitates soluble in excess of the reagent (133).

††† The color fades, with precipitate of S and reduction to ferrous salt (214).

†††† In solutions of normal acetates, hydrosulphuric acid gives precipitates (206, 279, 293).

††††† Much less soluble in acetic acid than al-amine-earth phosphates (216).

†††††† In case manganese is present as K<sub>2</sub>Mn<sub>2</sub>O<sub>8</sub> its occurrence in the second and third groups should always be prevented by previous reduction to a manganous salt by boiling with hydrochloric acid until the color disappears (237 b).



301. Separation of Third-Group Metals by  $\text{NH}_4\text{OH}$  with  $\text{NH}_4\text{Cl}$ , etc. (Phosphates, Oxalates, etc., being absent). (Explanation in 302.)

To the clear filtrate from Group II., in which  $\text{H}_2\text{S}$  will cause no precipitate, and freed from  $\text{H}_2\text{S}$  by boiling, add a few drops of **Nitric Acid** and boil an instant (to oxidize ferrous\*). Immediately add **Ammonium Chloride** and excess (153) of **Ammonium Hydroxide**. If there is a precipitate, filter and wash.

**Precipitate, Group III. A:  $\text{Fe}_2(\text{OH})_6$ ,  $\text{Cr}_2(\text{OH})_6$ ,  $\text{Al}_2(\text{OH})_6$ .**

Pierce the point of the filter, and with a little water wash the precipitate into a test-tube; add **Potassium or Sodium Hydroxide**, and boil for several minutes. If a residue remains, filter and wash.

**Precipitate:  $\text{Fe}_2(\text{OH})_6$ ,  $\text{Cr}_2(\text{OH})_6$ .**

**Solution:  $\text{K}_2\text{AlO}_4$ .**

*For Iron*, dissolve the precipitate in a little diluted **hydrochloric acid**, and test the solution (for  $\text{Fe}_2\text{Cl}_6$ ) with **potassium sulphocyanate** (217). If iron is present, this solution will give all the reactions of ferric iron.

Iron being found, to determine whether it is ferric or ferrous, or both,† in the original solution, test the latter, according to 221.

Study the characteristics of iron by use of the Table of Comparisons on the preceding page, the recapitulation in 221, and the text upon iron throughout.

*For Chromium*, test a portion of the precipitate, by fusing on platinum foil with **sodium or potassium nitrate** and **carbonate**, to change to *chromate*. Dissolve the mass ( $\text{Na}_2\text{CrO}_4$ ) in water; filter if necessary, acidify with acetic acid, and examine the clear solution for chromic acid, by 191-2-3.

Or oxidize by lead dioxide.

*If the original solution contains Chromate*, it also will give the reactions of chromic acid (191-2-3), and have a color mentioned in 189. If it contains *Chromic salt*—as  $\text{Cr}_2(\text{SO}_4)_3$ —it will give the reactions described in 181 and after.

*For Aluminium*, add to the potassium (or sodium) solution enough **hydrochloric acid** barely to acidulate it, and then add **ammonium carbonate**. A precipitate is  $\text{Al}_2(\text{OH})_6$ . (The result is obtained with nearly equal certainty by addition of excess of **ammonium chloride** to the alkaline solution, 167.)

Study aluminium as indicated in the Table of Comparisons, and in the text at 167 and after.

\* In the filtrate from the Second Group, iron is necessarily in the ferrous condition (214).

† Ferrous salts, which have been kept in the air, are never wholly free from ferric compounds (202).

Filtrate, Group III. B: Contains Zn, Ni, Co, Mn.

Add Ammonium Sulphide, and if a precipitate appears, warm until it subsides. Filter and wash. (This filtrate is to be examined for the Fourth Group.)

Precipitate: ZnS, NiS, CoS, MnS.

Treat, on the filter, with cold dilute Hydrochloric Acid. Note if a black residue remains. Boil the filtrate.

Residue: NiS, CoS* (black).		Solution: ZnCl <sub>2</sub> , MnCl <sub>2</sub> .
<p>For <i>Cobalt</i>, test the residue by the <b>blow-pipe</b> (269). The residue may be dissolved in a very little nitro-hydrochloric acid, and treated for the reactions stated in 268.</p> <p>In the study of cobalt, verify the reactions noted in the Table of Comparisons, and described in the text (264 and after).</p>	<p>For <i>Nickel</i>, test the residue by the <b>blow-pipe</b> (282). Then obtain reactions in the wet way, and separation from cobalt, by dissolving the residue in a very little nitro-hydrochloric acid, and treating by 280 and the adjacent text. (Cobalt is removed by one of the methods in 270.)</p>	<p>Add a decided excess of potassium or sodium hydrate, and digest without warming. Filter.</p>
	<p><b>Precipitate: Mn(OH)<sub>2</sub>*</b></p> <p>Test for <i>Manganese</i> by oxidations as by 248, 249, a; also, 250.</p> <p>The precipitate may be dissolved with hydrochloric acid, for reactions (242 and after; and Table of Comparisons).</p> <p>For acids of manganese, <b>Mn<sub>2</sub>vi</b> and (<b>Mn<sub>2</sub></b>)xiv, examine the original material by aid of 239.</p>	
		<p><b>Solution: K<sub>2</sub>ZnO<sub>2</sub></b></p> <p>Test for <i>Zinc</i> by adding ammonium sulphide: precipitate, <b>ZnS</b>.</p> <p>The reactions of zinc salts are obtained from the alkaline solution after acidulating it.</p> <p>Study the characteristics by aid of the Table of Comparisons, and the text at 292 and after.</p>

\* Small portions of cobalt and nickel may be dissolved from their sulphides by hydrochloric acid, and then will be precipitated with **Mn(OH)<sub>2</sub>**. This precipitate may be tested for **Co** and **Ni** by the blow-pipe, as above directed.

## SEPARATION OF THE THIRD-GROUP METALS.

**302.** The reactions of the seven important metals of the third group, as obtained with the compounds of each alone, include a sufficient number of distinct differences to construct several easy methods of complete separation. But it is more difficult to separate them when together than to distinguish them when apart, owing to the fact that the reactions of several of them are modified by the presence or action of others. In some of these cases, the interference is probably due to simple adhesion between the bases; in others, to chemical action of one base with another.

The division of the third group, by action of **ammonium chloride**, which dissolves manganous hydroxide, and excess of **ammonium hydroxide**, which dissolves cobalt, nickel, and zinc hydroxides, is indicated in the Table of Comparisons (300), and constitutes the first separation used in the Table at 301. If the excess of ammonium hydroxide be decided, the solution of the cobalt, nickel, and zinc will not fail. To dissolve the manganese, the ammonium salt must be added abundantly, and the metal must be in the manganous condition (242). Hence the oxidation of ferrous, by nitric acid, must be limited to addition of very little nitric acid with very brief boiling, to avoid the formation of manganic compounds.

The following precautions are essential to this method of separation: (a) All hydrosulphuric acid left from the second-group precipitation must be expelled. (b) Iron must be obtained in the ferric condition, as stated in the Table (301). (c) If citric and tartaric acids, sugar, albumen, and other organic substances which prevent precipitation by alkalies are present, they must be destroyed by evaporating the filtrate from the second group to dryness; adding a few drops of nitric acid, gently igniting, then dissolving in water acidulated with hydrochloric acid. A carbonaceous residue may be disregarded.

The separation of  $\text{Al}_2(\text{OH})_6$  from  $\text{Fe}_2(\text{OH})_6$ , and  $\text{Cr}_2(\text{OH})_6$ , by excess of fixed alkali, as directed in 301 A, requires that the alkali should be strong enough to dissolve the aluminium, and that the boiling should be sufficient to precipitate the chromium (181).

**303.** The separation of **CoS** and **NiS** from the other sulphides of Group III. B, as directed in the Table at 301, is not complete, as has been stated in a foot-note of the table. If acetic acid be employed instead of hydrochloric acid as a solvent, **CoS** and **NiS** will be left in the residue without waste; but now the **ZnS** will chiefly remain undissolved (293 and 300, under  $\text{H}_2\text{S}$ ). The separation of zinc from manganese can be done by treating their sulphides with acetic acid; also by treating their acetates with hydrosulphuric acid.

**304.** The following Plan of Separation, chiefly by excess of alkali hydroxides, may be employed as a study :

*Dissolve the third-group (ammonium sulphide) precipitate in hydrochloric acid with a very little potassium chlorate.*

In solution :  $\text{ZnCl}_2$ ,  $\text{Al}_2\text{Cl}_6$ ,  $\text{Cr}_2\text{Cl}_6$ ,  $\text{MnCl}_2$ ,  $\text{Fe}_2\text{Cl}_6$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ .

*Add ammonium chloride, then ammonium hydroxide in decided excess, and filter and wash.*

Residue (a) :  $\text{Fe}_2(\text{OH})_6$ ,  $\text{Al}_2(\text{OH})_6$ ,  $\text{Cr}_2(\text{OH})_6$ .

Solution (b) :  $\text{ZnO}$ ,  $\text{MnO}$ ,  $\text{CoO}$ ,  $\text{NiO}$  (as ammonio compounds).

*Dissolve residue (a) in hydrochloric acid ; add excess of potassium hydroxide in the cold. Filter.*

Precipitate (c) :  $\text{Fe}_2(\text{OH})_6$ . (Dissolve in acid and test.)

Solution (d) :  $\text{K}_2\text{Al}_2\text{O}_4$ ,  $\text{Cr}_2\text{O}_3(\text{K}_2\text{O})^n$ .

*Boil filtrate (d) for some time. Filter.*

Precipitate (e) :  $\text{Cr}_2(\text{OH})_6$ . (Test by fusion with alkali carbonate and nitrate.)

Solution (f) :  $\text{K}_2\text{Al}_2\text{O}_4$ . (Acidulate and test, 167, etc.)

To solution (b)—

*Add sulphide of ammonium ; filter and wash the precipitate formed. Digest with moderately dilute hydrochloric acid in the cold, and filter.*

Residue (g) :  $\text{CoS}$ ,  $\text{NiS}$ . (Test 301, B.)

Filtrate (h) :  $\text{ZnCl}_2$ ,  $\text{MnCl}_2$ .

*Boil filtrate (h) ; add excess of potassium hydroxide, and filter.*

Precipitate :  $\text{Mn}(\text{OH})_2$ . (Test by 249, a.)

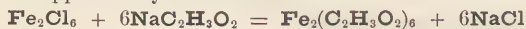
Solution :  $\text{K}_2\text{ZnO}_2$ . (Acidulate and test, 292, etc.)

In this plan—besides the difficulty with **manganese**, explained in 302—we have the difficult solution of **chromium** in cold, fixed alkali in presence of iron, and the uncertain solution of **aluminium** by alkali in presence of iron. Also, the separation of **cobalt** and **nickel**, both by redissolving in ammonium hydroxide, and by non-solution of their sulphides in hydrochloric acid, are processes requiring care, and affording only approximate separation.

**305.** The presence of **Phosphoric Acid** greatly complicates the analysis of the third group. Hence, the first proceeding with the filtrate of the second group is to ascertain whether it contains phosphoric acid or not. This is most conclusively done, as directed in the Table for Grouping, by the test with molybdate. It will be remembered, however, that a solution containing phosphoric acid along with any non-alkali bases must have an acid reaction. As soon as the solution is neutralized, phosphates are precipitated, and so phosphates are thrown down in third-group precipitations. As phosphoric is a non-volatile acid, it must be removed by precipitation. To separate it from bases, it must be precipitated from acid solution. This is done, *firstly*, as directed in the Table for “Analysis of Group III. when Phosphates are present” (see Part III.), by adding excess of ferric chloride, and then barium carbonate, in a very slightly acid solution. The  $\text{PO}_4$  is precipitated as ferric phosphate, with the other two pseudo-triads of the group, aluminium and chromium, both as hydrates. The phosphates of the pseudo-triads, especially ferric phosphate, are less easily dissolved by diluted acids or by acetic acid than any other metallic phosphates, except, perhaps, lead phosphate. In this way the dyad metals of the third and fourth groups are obtained in solution, free from  $\text{PO}_4$ , as they are not precipitated by barium carbonate. Now the precipitate of  $\text{Al}_2(\text{OH})_6$ ,  $\text{Cr}_2(\text{OH})_6$ ,  $\text{Fe}_2(\text{PO}_4)_2$ , etc., is boiled with excess of fixed alkali, which brings the aluminium into solution,

$\text{K}_2\text{Al}_2\text{O}_4$ , free from  $\text{PO}_4$ . The chromium is identified, in the very complex precipitate, by its oxidation to acid, and the color precipitates of chromate.

306. *Secondly*, the phosphoric acid radical can be separated from the alkaline earth metals, and from the dyads of the third group, by ferric salt in presence of *acetic acid* (307). There must be no other free acid; the ferric phosphate itself being soluble in hydrochloric and other strong acids. The acetic acid must be strong enough to prevent the precipitation of phosphates of calcium, etc.; and when of this strength it does dissolve some ferric phosphate, so that the separation is not very close. Ferric chloride being taken as a reagent, sodium acetate is used, so that the chlorine shall be neutralized as metallic salt, and not appear as hydrochloric acid:



In the following table this principle is employed, with certain precautions. Group III. A, is obtained by itself; then put with Group III. B, and digested with sulphide; because, it is claimed, in this way the phosphoric acid radical is combined with the pseudo-triads to a greater extent than when ammonium sulphide is brought to bear upon the whole group in solution. After the use of the sulphide, ferrosium may be present and again require oxidation, and the free chlorine used for this purpose also secures the solution of  $\text{CoS}$  and  $\text{NiS}$ . On digestion with *the acetate*, a precipitate must occur if  $\text{Fe}$ ,  $\text{Al}$ , or  $\text{Cr}$  is present. This precipitate may contain all these pseudo-triads, when it probably will not contain all the  $\text{PO}_4$ ; or it may contain all the  $\text{PO}_4$ , when it probably will not contain all the pseudo-triads. To assure the removal of all the  $\text{PO}_4$ , ferric salt is added. The filtrate is now free from phosphoric acid, and is to be treated essentially as directed for the third group when phosphates are absent—obtaining precipitates of Group III. A and B, and carrying the filtrate to the fourth group.



### 307. Separation of Third and Fourth Group Metals and Phosphoric Acid from each other, by Use of Alkali Acetate. (Explanation in 306.)

To the clear filtrate from Group II., freed from  $\text{H}_2\text{S}$  by boiling, add a few drops of **nitric acid**, and boil an instant; then at once precipitate by **ammonium chloride** and excess of **ammonium hydroxide**. Filter, and precipitate by **ammonium sulphide** (as directed in 301). Filter, and reserve this filtrate for Group IV.\* Wash both precipitates separately, and then digest them together, in an evaporating dish, with **ammonium sulphide**. Filter and wash.† [For **Ce**, **Be**, **U**, **Ti**, and **Tl**, see 310 and after.]

**Precipitate:**  $\text{FeS}$ ,  $\text{MnS}$ ,  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{ZnS}$ ;  $\text{Al}_2(\text{PO}_4)_3$ ,  $\text{Cr}_2(\text{PO}_4)_3$ ;  $\text{Al}_2(\text{OH})_6$ ,  $\text{Cr}_2(\text{OH})_6$ ; **Fa**, **Sr**, **Ca**, and **Mg Phosphates**. Dissolve the precipitate in a test-tube by hot dilute **hydrochloric acid**, with addition of a minute fragment of **potassium chlorate**. Digest to expel free chlorine, and filter out any free sulphur. Nearly neutralize with a dilute solution of sodium or potassium carbonate, and add solution of sodium or **Potassium Acetate** strongly acidified with **Acetic Acid**, as long as a precipitate results. Digest with gentle heat, and filter while hot.

<b>Precipitate:</b> $\text{Fe}_2(\text{PO}_4)_3$ , $\text{Al}_2(\text{PO}_4)_3$ , $\text{Cr}_2(\text{PO}_4)_3$ . Boil the precipitate, for some time, with <b>Potassium</b> or <b>sodium hydroxide</b> (free from <b>Al</b> ).		<b>Solution:</b> $[\text{Fe}_2\text{Cl}_6]$ , $[\text{Al}_2\text{Cl}_6]$ , $[\text{Cr}_2\text{Cl}_6]$ or $\text{H}_3\text{PO}_4$ ; $\text{MnCl}_2$ , $\text{CoCl}_2$ , $\text{NiCl}_2$ , $\text{ZnCl}_2$ ; $\text{BaCl}_2$ , $\text{SrCl}_2$ , $\text{CaCl}_2$ , $\text{MgCl}_2$ . Add <b>Ferric Chloride</b> , drop by drop, as long as a precipitate results, and until the liquid turns red, and digest, for some time, at gentle heat. Filter out and reject the precipitate, $\text{Fe}_2(\text{PO}_4)_3$ . Examine the filtrate for Third-Group bases and alkaline earths, in absence of $\text{PO}_4$ . This may be done as follows: To the filtrate (or solution not precipitated by ferric chloride) add <b>ammonium chloride</b> and <b>ammonium hydroxide</b> , and filter.	
<b>Residue:</b> $\text{Fe}_2(\text{PO}_4)_3$ , $\text{Cr}_2(\text{PO}_4)_3$ . (1) For <i>Chromium</i> , oxidize a portion of the residue (or of the precipitate before treatment with alkali), according to directions in the Table at 301. (2) For <i>Iron</i> , dissolve a portion of the residue (or of the precipitate before boiling with alkali) and test by <b>potassium sulphocyanate</b> .	<b>Solution:</b> $\text{K}_2\text{Al}_2\text{O}_4$ , with $\text{K}_2\text{PO}_4$ . Acidulate with <b>HCl</b> , and add excess of <b>ammonium hydroxide</b> . <b>Precipitate:</b> $\text{Al}_2(\text{PO}_4)_3$ , not soluble in acetic acid. To separate the aluminium from the $\text{PO}_4$ , fuse with silica, as directed in 169.	<b>Precipitate:</b> $\text{Al}_2(\text{OH})_6$ , $\text{Cr}_2(\text{OH})_6$ , $[\text{Fe}_2(\text{OH})_6]$ . Test for <i>Aluminium</i> and <i>Chromium</i> , as directed for Group III. A, in the Table at 301. For <i>Iron</i> , if not found in the precipitate by Acetate, test the original solution by 291.	<b>To the filtrate</b> add <b>Ammonium Sulphide</b> , and digest and filter. <b>Precipitate:</b> <b>MnS</b> , <b>CoS</b> , <b>NiS</b> , <b>ZnS</b> . Treat as directed for Group III. B, in the Table at 301.
		<b>Solution:</b> May contain <b>Ba</b> , <b>Sr</b> , <b>Ca</b> , <b>Mg</b> . Treat as directed in the Tables for Groups IV. and V.	

\* Alkaline earth metals, found in this filtrate, are in excess of the quantity held as phosphates.

† Phosphoric acid found here, shows that **Fe**, **Mn**, **Co**, and other Third-Group phosphates, had been formed, and then decomposed by the ammonium sulphide.

**308.** *Oxalates* have nearly the same deportment in the third group as phosphates, but the oxalic acid radical is decomposed altogether by the ignition and oxidation directed in 302 (c). By the same operation the fluorine of *fluorides* is expelled, and the silica of *silicates* left behind in the residue. *Boracic acid* is precipitated slightly in the third group of bases, but very little if ammonium chloride is added in large proportion.

**309.** The use of Barium Carbonate for separation of the pseudo-triads from the dyads of the third group has been described in 305, as used in the Table in Part III. The following is another scheme with use of this reagent:

#### Plan for Separation by Barium Carbonate.

Dissolve the third-group precipitate in hydrochloric acid with a little potassium chlorate (to oxidize ferrous); digest with gentle heat to expel all the free chlorine; neutralize with potassium carbonate; filter, if necessary; add the *barium carbonate*, agitate, and leave to subside in a flask or test-tube corked close to exclude the air. Decant, filter; wash with hot water.

Precipitate (a):  $\text{Fe}_2(\text{OH})_6$ ,  $\text{Cr}_2(\text{OH})_6$ , etc. (the excess of  $\text{BaCO}_3$ ).

Solution (b):  $\text{ZnCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ ; ( $\text{BaCl}_2$ ).

Dissolve precipitate (a) in dilute hydrochloric acid; add dilute sulphuric acid to complete the precipitate. Filter.

Precipitate:  $\text{BaSO}_4$ . (Reject.)

Solution (c):  $\text{Fe}_2\text{Cl}_6$ ,  $\text{Cr}_2\text{Cl}_6$ ,  $\text{Al}_2\text{Cl}_6$ .

Nearly neutralize solution (c) with potassium carbonate; add *excess of potassium hydroxide*, and boil for a few minutes. Filter.

Precipitate (d):  $\text{Fe}_2(\text{OH})_6$ ,  $\text{Cr}_2(\text{OH})_6$ .

Solution (e):  $\text{K}_2\text{Al}_2\text{O}_4$ . (Determine by 167.)

Fuse precipitate (d) with sodium carbonate and *nitrate*. Dissolve in hot water, and filter.

Residue (f):  $\text{Fe}_2(\text{OH})_6$ . (Dissolve in hydrochloric acid; test by 221.)

Solution (g):  $\text{K}_2\text{CrO}_4$ . (Test by 191, etc.)

To solution (b) add sulphuric acid to complete the precipitate; filter out the barium sulphate; nearly neutralize the filtrate with potassium carbonate; add *excess of potassium hydroxide*; boil a very short time, and filter.

Solution (h):  $\text{K}_2\text{ZnO}_2$ . (Add hydrosulphuric acid, 293.)

Precipitate (i):  $\text{Mn}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$ .

Wash precipitate (i), dissolve in a little dilute hydrochloric acid, nearly neutralize with ammonium hydroxide; add ammonium acetate, and *treat thoroughly with hydrosulphuric acid*. Filter.

Precipitate (j):  $\text{CoS}$ ,  $\text{NiS}$ .

Solution (k):  $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$ . (Add ammonium hydrate and sulphide—242, etc.)

Dissolve precipitate (j) in hydrochloric acid with a little potassium chlorate; nearly neutralize with potassium carbonate; add solution of *potassium cyanide*, sufficient barely to redissolve the precipitate at first produced. Boil thoroughly, cool, and filter; add strong solution of good *sodium hypochlorite*, leave for some time in a warm place (as long as a black precipitate continues to form), and filter (281).

Precipitate (l):  $\text{Ni}_2(\text{OH})_6$ .

Solution (m):  $\text{K}_6\text{Co}_2(\text{CN})_{12}$ . (Evaporate to dryness; test by 263, etc.)

CERIUM.  $Ce = 140.424$ .

**310. Specific gravity**, electrolytic, 6.628 ; after fusion, 6.728 (HILLEBRAND and NORTON, 1875). Melting point between silver and antimony. Its principal source is cerite, in which it is found as a silicate, in conjunction with lanthanum and didymium. It is prepared (1) by fusing  $Ce_2Cl_6$  with  $Na$  (WÖHLER, 1867), and (2) by electrolysis of  $Ce_2Cl_6$  (HILLEBRAND and NORTON, 1875). **Properties.**—The metal has a steel-gray color ; burns in gaseous  $Cl$ ,  $Br$ ,  $I$ ,  $S$ , and  $P$ . Is not dissolved by cold concentrated  $HNO_3$  or  $H_2SO_4$  ; easily dissolved by dilute  $HCl$ ,  $HNO_3$ , and  $H_2SO_4$ . When ignited it burns in the air with greater brilliancy than  $Mg$ . Cold, dry air has no action upon it ; moist air tarnishes it slightly. The **oxides** are  $Ce_2O_3$ ,  $CeO_2$ , and  $CeO_3$ . Cerous oxide ( $Ce_2O_3$ ) is made by heating the oxalate or carbonate in  $H$ . *Cerous hydroxide*,  $Ce_2(OH)_6$ , is formed by treating cerous salts with fixed alkalis. It is white, soon becoming yellow by oxidation. *Ceric oxide* ( $CeO_2$ ) is formed when  $Ce$ ,  $Ce_2(OH)_6$ ,  $Ce_2(CO_3)_3$ ,  $Ce_2(SO_4)_3$ ,  $Ce_2(NO_3)_6$ , or  $Ce_2(C_2O_4)_3$  is ignited in the air. It is yellow, as is also the hydroxide formed by treating  $Ce_2(OH)_6$  with  $Cl$  in presence of  $KOH$ . Ceric hydroxide loses water in drying, and becomes  $Ce_2O(OH)_6$ . *Cerium peroxide*,  $CeO_3$ , is formed by treating  $Ce_2(SO_4)_3$  with  $H_2O_2$  in presence of  $NH_4OH$  (BOISBAUDRAN, 1885). Other oxides of cerium have been described, but their existence is doubtful. The only stable *salts* of cerium are the *cerous*. *Ceric* salts are reduced to cerous salts by boiling, with evolution of oxygen ; the one best known is  $Ce(SO_4)_2$ .

**Reactions of Cerous Salts.**—**Potassium** or sodium hydroxide precipitates from cerous salts the hydroxide,  $Ce(OH)_3$ , white ; changing by chlorine or other oxidizing agents to ceric hydroxide, yellow.—**Ammonium hydroxide** precipitates a basic salt. Alkalis do not redissolve their precipitates.—Alkaline **carbonates** precipitate white cerous *carbonate*,  $Ce_2(CO_3)_3$ .—**Oxalates** precipitate cerous oxalate, white ; first gelatinous, then crystalline, converted by ignition into ceric oxide.—**Potassium Sulphate** precipitates potassio-cerous sulphate,  $(K_2SO_4)_3Ce_2(SO_4)_3$ , white, crystalline, insoluble in excess.—**Ferrocyanides** precipitate white cerous ferrocyanide.—Hydrosulphuric acid **separates** from cerium the metals of the second group ; saturated solution of potassium sulphate separates cerium from zinc, chromium, manganese, iron, cobalt, nickel ; also from the earth metals.—Barium Carbonate precipitates cerous salts completely on boiling, not at all when cold. The reaction with oxalic acid is characteristic.—With borax and microcosmic salt, all compounds of cerium give, with the oxidizing **blow-pipe** flame, a bead, deep red while hot, colorless when cold ; with the reducing flame, when strongly saturated, a yellow enamelled bead.

BERYLLIUM.  $Be = 9.085$ .

**311. Specific gravity**, 1.85 (HUMIDGE, 1885). Melts above the point at which  $NaCl$  readily volatilizes (NILSON and PETERSSEN, 1878).

**Occurrence.**—Only in combination, in beryl,  $Be_3Al_2(SiO_3)_6$ , and in some

other silicates, also in chrysoberyl,  $\text{BeOAl}_2\text{O}_3$ . Prepared by fusion of  $\text{Be}_2\text{Cl}_6$  with **K** or **Na**. It has not yet been reduced by electrolysis, by carbon, or by hydrogen. **Properties**.—Steel-colored, hard, malleable, unchanged in ordinary air, only slightly tarnished in the air at a red heat, but burns in the oxyhydrogen flame; burns in **Cl**, soluble in **HCl** and  $\text{H}_2\text{SO}_4$ , and very slowly in  $\text{HNO}_3$ ; soluble in **KOH** and **NaOH**, but not in  $\text{NH}_4\text{OH}$ . **Oxide and Hydroxide**.—The oxide,  $\text{Be}_2\text{O}_3$ , is formed by ignition of the hydroxide or any of its oxysalts, except those with non-volatile acids. The hydroxide,  $\text{Be}_2(\text{OH})_6$ , is formed by precipitation with  $\text{NH}_4\text{OH}$  and drying at  $100^\circ \text{C}$ .

**Reactions of Beryllium Salts**.—Fixed alkali hydroxides precipitate the hydroxide,  $\text{Be}(\text{OH})_2$ , resembling aluminium hydrate, soluble in excess; ammonium hydroxide causes the same precipitate, insoluble in excess or in cold solution of ammonium salts.—Alkali sulphides also precipitate the hydroxide.—Carbonates precipitate double carbonates, or basic carbonates of beryllium, soluble in ammonium carbonate. Barium carbonate does not precipitate  $\text{Be}_2\text{Cl}_6$  in cold solutions, but does precipitate it completely at  $100^\circ \text{C}$ .—Phosphates throw down  $\text{BeHPO}_4$ , flocculent. Oxalates cause no precipitate.—Ferrocyanide of potassium causes, after some time, a gelatinous precipitate.—Beryllium is separated and distinguished from aluminium, and from zinc, by the solubility of its hydroxide and carbonate in excess of ammonium carbonate; from zinc by the indifference of its alkaline solutions to ammonium sulphide. Dilute alkaline solutions precipitate on long boiling, also the hydroxide dissolves in ammonium chloride solution on boiling, both distinctions from aluminium.—Beryllium compounds, ignited with cobalt nitrate, yield a gray mass. Soluble salts of beryllium have a sweet taste.

## URANIUM. $\text{U} = 238.482$ .

**312.** *Specific gravity*, 18.685 (ZIMMERMANN, 1882). Melts at a bright red heat (PELIGOT, 1868).

**Occurrence**.—Found in various minerals; its chief ore is pitch-blende, which contains from 40 to 90 per cent. of  $\text{U}_3\text{O}_8$ . **Preparation**.—By fusing  $\text{UCl}_4$  with **K** or **Na**. **Properties**.—It has the color of nickel, hard, but softer than steel, malleable, permanent in the air and water at ordinary temperatures; when ignited burns to  $\text{U}_3\text{O}_8$ ; unites directly with **Cl**, **Br**, **I**, and **S** when heated; soluble in **HCl**,  $\text{H}_2\text{SO}_4$ , and slowly in  $\text{HNO}_3$ . **Oxides and Hydroxides**.—*Uranous oxide* ( $\text{UO}_2$ ), formed by igniting the higher oxides in carbon or hydrogen, is a brown powder, soon turning yellow by absorption of oxygen from the air. *Uranous hydroxide* is formed by precipitating uranous salts with alkalis. *Uranic oxide*,  $\text{UO}_3$ , is formed by heating uranic nitrate cautiously to  $25^\circ \text{C}$ ., and upon ignition in the air both this and other uranium oxides, hydroxides, and uranium oxysalts with volatile acids are converted into  $\text{U}_3\text{O}_8 = \text{UO}_2 \cdot 2\text{UO}_3$ . **Uranous Salts**.—Uranium acts as a base in two classes of salts, *uranous* and *uranyl* salts. *Uranous* salts are green and give green solutions, from which alkalis precipi-



tate uranous hydroxide, insoluble in excess of the alkali; alkali carbonates precipitate  $\text{U}(\text{OH})_4$ , soluble in  $(\text{NH}_4)_2\text{CO}_3$ ; with  $\text{BaCO}_3$  the precipitation is complete even in the cold.  $\text{H}_2\text{S}$  is without action;  $(\text{NH}_4)_2\text{S}$  gives a dark-brown precipitate;  $\text{K}_4\text{Fe}(\text{CN})_6$  gives a reddish-brown precipitate. In their action toward oxidizing and reducing agents uranous and uranyl (uranic) salts resemble closely ferrous and ferric salts; uranous salts are even more easily oxidized than ferrous salts—*e.g.*, by exposure to the air, by  $\text{HNO}_3$ ,  $\text{Cl}$ ,  $\text{HClO}_3$ ,  $\text{Br}$ ,  $\text{K}_2\text{Mn}_2\text{O}_8$ , etc. Gold, silver, and platinum salts are reduced to the free metal. **Uranyl Salts.**—The hexad uranium ( $\text{U}^{\text{VI}}$ ) acts as a base, but usually forms basic salts, never normal: we have  $\text{UO}_2(\text{NO}_3)_2$ , not  $\text{U}(\text{NO}_3)_6$ ;  $\text{UO}_2\text{SO}_4$ , not  $\text{U}(\text{SO}_4)_3$ . These basic salts were formerly called uranic salts, but at present ( $\text{UO}_2$ )<sup>+</sup> is regarded as a basic radical and called *uranyl*, and its salts are called uranyl salts—*e.g.*,  $\text{UO}_2\text{Cl}_2$  uranyl chloride,  $(\text{UO}_2)_3(\text{PO}_4)_2$  uranyl orthophosphate. Solutions of uranyl salts are yellow;  $\text{KOH}$  and  $\text{NaOH}$  give a yellow precipitate, consisting of  $\text{K}_2\text{U}_2\text{O}_7$  and  $\text{Na}_2\text{U}_2\text{O}_7$ , insoluble in excess. Alkali carbonates give a yellow precipitate, soluble in excess;  $\text{BaCO}_3$  and  $\text{CaCO}_3$  give  $\text{UO}_3$ .  $\text{H}_2\text{S}$  does not precipitate the uranium, but slowly reduces uranyl salts to uranous salts (ARENDT and KNOP).  $(\text{NH}_4)_2\text{S}$  gives a dark-brown precipitate.  $\text{K}_4\text{Fe}(\text{CN})_6$  gives a reddish-brown precipitate. Sodium phosphate gives a yellow precipitate.  $\text{Zn}$ ,  $\text{Cd}$ ,  $\text{Sn}$ ,  $\text{Pb}$ ,  $\text{Co}$ ,  $\text{Cu}$ ,  $\text{Fe}$ , and ferrous salts reduce uranyl salts to uranous salts. **Uranates.**—The hexad uranium acts as an acid toward some stronger bases. Thus we have  $\text{K}_2\text{U}_2\text{O}_7$  and  $\text{Na}_2\text{U}_2\text{O}_7$ , formed by precipitating uranyl salts with  $\text{KOH}$  and  $\text{NaOH}$ ; compare the similar salts of the hexad chromium,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{Na}_2\text{Cr}_2\text{O}_7$ . Other oxides of uranium are described, but are doubtless combinations of  $\text{UO}_2$  and  $\text{UO}_3$ .

### TITANIUM. Ti = 47.980.

**313.** Titanium is never found in a free state; found in ilmenite,  $\text{Fe}_2\text{Ti}_2\text{O}_3$ , in rutile, brookite, and anatase. It is prepared by heating the chloride or fluoride with  $\text{K}$  or  $\text{Na}$ . It is a dark gray powder. When burned, combines with both the  $\text{N}$  and  $\text{O}$  of the air; soluble in  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$ . It forms very stable compounds with nitrogen and cyanogen (furnace products); it decomposes water at the boiling temperature. In its most stable compounds it acts as a tetrad: titanic oxide,  $\text{TiO}_2$ , acting as an *acidulous anhydride* toward bases and having properties and salts resembling those of silicic acid—likewise forming a full series of (quadrivalent) *titanic salts*, as  $\text{TiCl}_4$ . The metal also acts as a pseudo-triad, in *titanous* oxide,  $\text{Ti}_2\text{O}_3$ , titanous chloride,  $\text{Ti}_2\text{Cl}_6$ , and a few other salts, all powerful reducing agents.

*a.* **Titanous salts** make violet-colored solutions (the chloride, nitrate, and sulphate dissolve in water), from which **alkali hydroxides** and their **carbonates** precipitate titanous hydroxide,  $\text{Ti}_2\text{O}_3(\text{H}_2\text{O})_x$ , dark brown, changing in the air to titanic acid,  $\text{H}_2\text{TiO}_3$ ; ammonium **sulphide** throws down the same precipitate, hydrosulphuric acid producing no change; calcium carbonate separates the hydroxide.—Ferric and cupric salts are reduced to ferrous and cuprous compounds, and from salts of mercury, silver, and gold



the metals are separated, by titanous salts, which are thereby changed to titanic compounds.

*b. Titanic salts* are mostly insoluble in **water**, or decomposed by it with precipitation of titanic acid,  $\text{H}_2\text{O} \cdot \text{TiO}_2$  or  $\text{H}_2\text{TiO}_3$ . Of this compound there are *two modifications*, one soluble and one insoluble in hydrochloric and nitric acids; strong sulphuric acid dissolves both modifications; but the titanic sulphate is decomposed and precipitated on dilution, and the chloride on long boiling (distinctive). Titanic chloride,  $\text{TiCl}_4$ , and nitrate,  $\text{Ti}(\text{NO}_3)_4$ , are permanently soluble in water.—From these, **Alkalies** and their **carbonates** and **sulphides** throw down the white voluminous *titanic hydrate* or titanic acid, insoluble in excess of the precipitants, and in ammonium salts; the same precipitate is produced by **barium carbonate**. **Ferrocyanide** of potassium gives a dark-brown precipitate of titanic ferrocyanide; **tannic acid**, an orange precipitate.

*c. Titanates*, as shown above, are not formed by treating titanic acid, even when recent, with aqueous alkalies, but are produced by fusion of titanic acid with alkalies or their carbonates. So prepared, the neutral alkali titanates have a yellow color, and are decomposed by hot water with separation of insoluble acid titanates of the same bases, but soluble in acids as titanic salts.

*d. Compounds of titanium acids* with **microcosmic salt** dissolve in the outer flame to a clear **bead**, pale yellow when hot, and colorless when cold. The strong reducing flame now turns the bead yellow while hot (reddish when cooling), and *violet* when cold (titanous oxide). If sulphate of iron be added, the bead by the inner flame is blood-red. In the borax bead the same reactions are obtained, less intense.—**Ignition** on charcoal with soda does not reduce titanium to the metallic state (distinction from tin).

### THALLIUM. $\text{Tl} = 203.715$ .

**314.** *Specific gravity of the wire*, 11.91 (CROOKES, 1864). *Melting point*,  $293.9^\circ \text{C}$ . ( $561^\circ \text{F}$ .) (CROOKES, 1864). Is found in crookesite and in many varieties of iron and copper pyrites. **Preparation**.—(1) By electrolysis. (2) By reduction from its solutions by **Zn** or **Al**. (3) By fusion with **KCN**. (4) By fusion of the oxalate or with some other form of carbon. (5) Fusion in hydrogen gas reduces it with difficulty. It is a bluish-white metal, softer than lead, malleable and ductile; tarnishes rapidly in the air; may be preserved under water, which it does not decompose below a red heat; soluble in  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , in **HCl** with great difficulty; combines directly with **Cl**, **Br**, **I**, **P**, **S**, **Se**, and precipitates from their solutions **Cu**, **Ag**, **Hg**, **Au**, and **Pb** in the metallic state.

**Reactions**.—As a monad its compounds are stable, and not easily oxidized; as a triad it is easily reduced to the univalent condition

*a. Thallous oxide*,  $\text{Tl}_2\text{O}$ , is black; on contact with water it forms an hydroxide,  $\text{TlOH}$ , freely soluble in water and in alcohol, to colorless solutions. The carbonate is soluble in about 20 parts of water; the sulphate and phosphate are soluble; the chloride very sparingly soluble; the iodide insoluble in water. **Hydrochloric acid** precipitates, from solutions not very dilute, *thallous chloride*,  $\text{TlCl}$ , white, and unalterable in the air. As a first-group precipitate, thallous chloride dissolves enough in hot water to give the light yellow precipitate of *iodide*, **TII**, on adding a drop of **potassium iodide** solution—the precipitate being slightly soluble in excess of the reagent.  $\text{H}_2\text{S}$  precipitates the ace-

tate; but not the acidified solutions of its other salts.  $(\text{NH}_4)_2\text{S}$  precipitates  $\text{Tl}_2\text{S}$ , which, on exposing to the air, soon oxidizes to sulphate. **Ferrocyanides** give a yellow precipitate,  $\text{Tl}_4\text{Fe}$ ; **phosphomolybdic acid** a yellow precipitate; and potassium **permanganate**, a red-brown precipitate, consisting in part of  $\text{Tl}_2\text{O}_3$ . **Chromates** precipitate yellow, normal chromate; and **platinic chloride**, pale orange, *thallious platinic chloride*,  $(\text{TlCl})_2\text{-PtCl}_4$ . Thallium compounds readily impart an intense green color to the **flame**, and one emerald-green line to the **spectrum** (the most delicate test). The flame-color and spectrum, from small quantities, are somewhat evanescent, owing to rapid vaporization.

*b.* **Thallic oxide**,  $\text{Tl}_2\text{O}_3$ , dark violet, is insoluble in water; the hydroxide, an oxyhydroxide,  $\text{TlO}(\text{OH})$ , is brown and gelatinous. This hydroxide is precipitated from thallic salts by the caustic **alkalies**, and not dissolved by excess. **Chlorides** and **bromides** do not precipitate thallic solutions; **iodides** precipitate  $\text{TlI}$  with **I**. **Sulphides**, and  $\text{H}_2\text{S}$ , precipitate *thallious sulphide*, with sulphur. Thallic oxide, suspended in solution of potassium hydroxide, and treated with **chlorine**, develops an intense violet-red color. Thallic chloride and sulphate are reduced to thallious salts by boiling their water solutions.

**315. YTTERBIUM.**  $\text{Yb} = 172.761$ .—In 1878 MARIGNAC prepared the sulphate,  $\text{Yb}_2(\text{SO}_4)_3$ , the oxalate,  $\text{Yb}_2(\text{C}_2\text{O}_4)_3$ , the nitrate, and some other ytterbium salts. The metal has not been isolated.

**316. TERBIUM.**  $\text{Tr} = 148.5?$ —Terbium oxide,  $\text{Tr}_2\text{O}_3$ , occurs in samarskite; the sulphate,  $\text{Tr}_2(\text{SO}_4)_3$ , and a few other salts, have been prepared, but as the metal has not been isolated the composition of its salts is not certain.

**317. SCANDIUM.**  $\text{Sc} = 43.98$ .—Scandium oxide,  $\text{Sc}_2\text{O}_3$ , is found in gadolinite; the sulphate,  $\text{Sc}_2(\text{SO}_4)_3$ , the oxalate,  $\text{Sc}_2(\text{C}_2\text{O}_4)_3$ , and a few other salts, have been prepared; the metal has not been isolated.

**318. SAMARIUM.**  $\text{Sm} = 148.801$ .—Discovered by BOISBAUDRAN in samarskite by its peculiar spectrum. The oxide,  $\text{Sm}_2\text{O}_3$ , the chloride,  $\text{SmCl}_3$  or  $\text{Sm}_2\text{Cl}_6$ , the sulphate, the nitrate, and a few other salts, have been prepared. The metal has not been isolated.

**319. GALLIUM.**  $\text{Ga} = 68.584$ .—*Specific gravity*, 5.9. *Melting point*,  $30.15^\circ \text{ C.}$  ( $86.27^\circ \text{ F.}$ ) Found in zinc-blende. **Prepared** by electrolysis. It is a soft metal, may be cut with a knife, flexible and malleable, soluble in  $\text{HCl}$  and  $\text{KOH}$ , and in hot  $\text{HNO}_3$ . The oxide,  $\text{Ga}_2\text{O}_3$ , the chloride,  $\text{Ga}_2\text{Cl}_6$ , and sulphate are best known.

**320. DECIPIUM.**  $\text{Dp} = 171.?$ —Discovered by DELAFONTINE in samarskite by means of the spectroscope. The oxide,  $\text{Dp}_2\text{O}_3$ ,  $\text{Dp}_2(\text{SO}_4)_3$ ,  $\text{Dp}_2(\text{IO}_3)_6$ ,  $\text{Dp}_2(\text{C}_2\text{H}_3\text{O}_2)_6$ , and  $\text{Dp}_2(\text{C}_2\text{O}_4)_3$  are best known. The metal has not been isolated.

321. The leading reactions of the remaining rare metals of the Third Group are given in the following Comparative Table. The six metals first named form *earthy* oxides; tantalum and niobium, like titanium, form acids. Indium and vanadium, also forming acids, can be placed in the Second Group.

	Zr	Th	Y	E	La	D	Ta	Nb	In	V
$\text{NH}_4\text{OH}$ with $\text{NH}_4\text{Cl}$	$\text{Zr}(\text{OH})_4$	$\text{ThO}(\text{OH})_2$	$\text{Y}_2(\text{OH})_6$ §	Basic salt.	$\text{La}_2(\text{OH})_6$	$\text{D}_2(\text{OH})_6$ *	$\text{HTaO}_3$	Pre. **	$\text{In}_2(\text{OH})_6$	¶¶
$(\text{NH}_4)_2\text{S}$	$\text{Zr}(\text{OH})_4$	$\text{ThO}(\text{OH})_2$	$\text{Y}_2(\text{OH})_6$	Basic salt.	$\text{La}_2(\text{OH})_6$	Pre. *	$\text{HTaO}_3$	Pre. **	$\text{In}_2\text{S}_3$ §§	
$\text{KOH}$ or $\text{NaOH}$ , excess.	Pre.	Pre.	Pre.	$\text{E}_2(\text{OH})_6$	Pre. ¶	Pre.	††	††	Sol. †	
$\text{K}_2\text{CO}_3$ , excess.	Sol. * †	Sol. †	Pre. *	Pre. *	Pre.	Pre.	.....	.....	Pre.	
$(\text{NH}_4)_2\text{CO}_3$ , excess.	Sol. †	Sol. †	Sol. *	Sol. *	Pre.	Pre.	.....	.....	Sol. *	
$\text{BaCO}_3$ , cold.	Pre. *	Pre.	No pre.	No pre.	Pre.	Pre.	.....	.....	Pre.	
$\text{K}_2\text{SO}_4$	Pre.	Pre. †	No pre.	No pre. †	Pre. *	Pre.	.....	.....	.....	
$\text{H}_2\text{C}_2\text{O}_4$	Pre.	Pre.	Pre.	Pink pre.	Pre.	Pre.	.....	.....	.....	
$\text{K}_4\text{Fe}(\text{CN})_6$	.....	Wt. pre.	Wt. pre.	.....	.....	Wt. pre.	.....	No pre.	Pre. *	Green pre.
$\text{K}_6\text{Fe}_3(\text{CN})_{12}$	.....	No pre.	No pre.	.....	.....	.....	.....	Red pre.	Wt. pre.	
$\text{Na}_2\text{S}_2\text{O}_3$	Pre.	Pre. *	No pre.	.....	.....	No pre.	.....	Yel. pre.	.....	

\* In part.

† Reprecipitated on boiling.

‡ In boiling, concentrated solutions, slowly but completely.

§ Slightly soluble in ammonium chloride.

\*\* Contains  $\text{NH}_4\text{OH}$ .

¶ Partial pre. in the cold, dissolving when warm.

†† When the acetate is precipitated by excess of ammonia, and the washed precipitate treated with iodine, a blue color appears.

‡‡ Fusion with  $\text{KOH}$  gives  $\text{KTaO}_3$ , soluble in water; with  $\text{NaOH}$ ,  $\text{NaTaO}_3$ , insoluble in solution of sodium hydroxide. The sol. of  $\text{KTaO}_3$  is pre. by  $\text{CO}_2$ ; also by  $\text{HCl}$  (as  $\text{Ta}_2\text{O}_5$ ) soluble in excess.

§§ Solutions of niobates, as  $\text{KNbO}_3$ , are pre. by mineral acids, as  $\text{HNO}_3$ . In acidulated solutions, zinc forms a blue color (characteristic), lower oxide being formed.

|| Formed yellow, in slightly acid solutions, by  $\text{H}_2\text{S}$ , soluble in excess of  $(\text{NH}_4)_2\text{S}$ , and in  $\text{HCl}$ .

¶¶ In neutral solutions, a brown color; on acidulating, a brown pre.,  $\text{V}_2\text{S}_5$ .  $\text{H}_2\text{S}$  reduces vanadates to  $\text{V}_2\text{O}_3$ , with blue color. Acid solutions of  $\text{V}_2\text{O}_3$  are green; of  $\text{V}_2\text{O}_5$ , red.

¶¶ For the characteristics of the several conditions of this element, see *Watts' Dictionary*, Vols. V. and VI., and *Gmelin's Handbuch*, 2, 227

## GROUPS I. AND II.

**322.** The first group includes metals whose chlorides are insoluble in water (**Pb**, **Ag**, and (**Hg<sub>2</sub>**)").

The second group includes those metals whose chlorides are soluble in water, but whose sulphides are insoluble in dilute acids.

Copper.....	<b>Cu</b> = 63.173	Gold.....	<b>Au</b> = 196.155
Bismuth.....	<b>Bi</b> = 207.523	Platinum.....	<b>Pt</b> = 194.415
Cadmium.....	<b>Cd</b> = 111.835	Palladium.....	<b>Pd</b> = 105.737
Lead.....	<b>Pb</b> = 206.471	Ruthenium.....	<b>Ru</b> = 104.217
Silver.....	<b>Ag</b> = 107.675	Iridium.....	<b>Ir</b> = 192.651
Mercury.....	<b>Hg</b> = 199.712	Rhodium.....	<b>Rh</b> = 104.055
Arsenic.....	<b>As</b> = 74.918	Osmium.....	<b>Os</b> = 198.494
Antimony.....	<b>Sb</b> = 119.955	Tellurium.....	<b>Te</b> = 127.960
Tin.....	<b>Sn</b> = 117.698	Selenium.....	<b>Se</b> = 78.797
		Tungsten.....	<b>W</b> = 183.610
		Molybdenum.....	<b>Mo</b> = 95.527
		Norwegium.....	<b>Ng</b> = 218.93?
		Germanium.....	<b>Gr</b> = 72.32

**323. COMPARATIVE VIEW.**—Owing to the partial solubility of lead chloride in water, it is never completely precipitated in the first group; hence it must also be tested for in the second group. (**Hg<sub>2</sub>**)" belongs to the first group and **Hg**" to the second. Silver, then, is the only exclusively first-group metal.

**324.** The metals included in these groups are **less strongly electro-positive** than those of the other groups. Only bismuth, antimony, tin, and molybdenum decompose water, and these only slowly and at high temperatures. The oxides of silver, mercury, gold, platinum, and palladium are decomposed below a red heat. Copper, lead, and tin tarnish by oxidation in the air. In general, these metals either do not dissolve in acids with evolution of hydrogen, or do so with difficulty. Nitric acid is the best solvent for all, except antimony and tin, which are rapidly oxidized by it.

**325.** Mercury, arsenic, antimony, and tin form, each, two stable classes of salts. Therefore, the lower oxides, chlorides, etc., of these metals act as reducing agents; and their higher oxides, chlorides, etc., as oxidizing agents, each to the extent of its chemical force. Arsenic, antimony, tin, molybdenum, and several of the rare metals of these groups enter into *acidulous* radicals, which form stable salts. Arsenic and selenium are metalloids rather than metals. Arsenic, antimony, and bismuth belong to the Nitrogen Series of Elements.

**326.** A large proportion of the compounds of these metals are **insoluble** in water. Of the oxides or hydroxides, only the acids of arsenic are soluble in water. The only insoluble chlorides, bromides, and iodides are in these groups. The sulphides, carbonates, oxalates, phosphates, borates, and cyanogen compounds are insoluble. Most of the so-called soluble compounds



of bismuth, antimony, and tin, and some of those of arsenic and mercury, dissolve only in acidulated water, being decomposed by pure water, with formation of insoluble basic salts.

**327.** The oxides of arsenic, antimony, and tin—in general terms—**dissolve in alkali hydroxides**. Oxides of silver, copper, and cadmium dissolve in ammonium hydroxide; oxide of lead, in fixed alkali hydroxide. Metallic lead, like zinc, dissolves in fixed alkali hydroxide, with evolution of hydrogen, though it scarcely decomposes any acid by displacing hydrogen.

**328.** Many **double salts** are formed with the metals of this group. Those whose sulphides dissolve in alkali sulphides, owe this property to the formation of soluble sulpho-salts or double sulphides. Platinum forms a large number of stable double chlorides, soluble and insoluble; and gold forms double chlorides, cyanides, etc.

**329.** Mercury, antimony, silver, and gold do not form **hydroxides**. The oxides of gold are very instable.

**330.** The metals of this group are all easily reduced to the metallic state by **ignition on charcoal**. Except mercury and arsenic, which *vaporize*, and certain rarer metals difficultly fusible, the reduced metals melt to metallic grains on the charcoal. Mercury and antimony vaporize from the liquid, arsenic from the solid state.

### COPPER. $\text{Cu} = 63.173$ .

**331.** *Specific gravity*, variable: hammered, 8.9587 (BERZELIUS); crystallized, 8.94; electrolytic, 8.914 (MARCHAND). *Melting point*, variable; VIOLE finds it to be  $1054^{\circ} \text{C}$ . ( $1929^{\circ} \text{F}$ .) Valence, a dyad in cupric salts, as  $\text{Cu}''\text{Cl}_2$ , and a pseudo-monoad in cuprous salts, as  $(\text{Cu}_2)'\text{Cl}_2$ .

**332. Occurrence.**—Copper is found native in various parts of the world, and especially in the region of Lake Superior. The most important English ore is copper pyrites,  $\text{CuFeS}_2$ ; copper glance is  $\text{Cu}_2\text{S}$ ; green malachite is  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ; blue malachite is  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ ; red copper ore is  $\text{Cu}_2\text{O}$ ; tenorite is  $\text{CuO}$ ; it is found in many other ores, and is utilized as a by-product in their reduction.

**333. Preparation.**—For the details of the various methods of copper-smelting the works on metallurgy should be consulted. In the laboratory pure copper may be produced (1) by electrolysis; (2) reduction by ignition in hydrogen gas; (3) reduction of the oxide by ignition with carbon, carbon monoxide, illuminating gas, or other forms of carbon; (4) reduction of the oxide by **K** or **Na** at a temperature a little above the melting point of these metals; (5) reduction by fusion with potassium cyanide ( $2\text{CuO} + 2\text{KCN} = 2\text{Cu} + 2\text{KCNO}$ ). For its reduction in the humid way see 351.



**334. Properties.**—A red metal, but thin sheets transmit a greenish-blue light, and it also shows the same greenish-blue tint when in a molten condition. Of the metals in ordinary use only gold and silver exceed it in malleability. In ductility it is inferior to iron and cannot be so readily drawn into exceedingly fine wire. Although it ranks next to iron in tenacity, its wire bears about half the weight which an iron wire of the same size would support. As a conductor of heat it is surpassed only by gold. Next to silver it is the best conductor of electricity. Dry air has no action upon it; in moist air it becomes coated with a film of oxide which protects it from further action of air or of water.

**335. Oxides and Hydroxides.**—*Cuprous oxide* ( $\text{Cu}_2\text{O}$ ) is found native; it is prepared (1) by reducing  $\text{CuO}$  by means of grape-sugar in alkaline mixture; (2) by igniting  $\text{CuO}$  with metallic copper; (3) by treating an ammoniacal cupric solution with metallic copper, then adding  $\text{KOH}$  and drying. A red powder, soluble in  $\text{HCl}$ , forming  $\text{Cu}_2\text{Cl}_2$ . *Cuprous hydroxide* is formed by precipitating cuprous salts with  $\text{KOH}$  or  $\text{NaOH}$ . *Cupric oxide* is formed by igniting the hydroxide, carbonate, sulphate, nitrate, and some other cupric salts in the air. *Cupric hydroxide* is formed by precipitating cupric salts with  $\text{KOH}$  or  $\text{NaOH}$ . It is stated by H. ROSE that *tetracupric monoxide* ( $\text{Cu}_4\text{O}$ ) is formed by treating a cupric salt with  $\text{KOH}$  and a quantity of  $\text{K}_2\text{SnO}_2$  insufficient to reduce it to the metallic state. A *peroxide* of copper ( $\text{CuO}_2$ ) is supposed to be formed by treating  $\text{Cu(OH)}_2$  with  $\text{H}_2\text{O}_2$  at  $0^\circ \text{C}$ .

**336. Solubilities.**—Copper does not dissolve in acids with evolution of hydrogen; it dissolves most readily in nitric acid, chiefly with the evolution of nitric oxide (*a*); also, in hot concentrated sulphuric acid, with evolution of sulphurous anhydride (*b*):



The atmosphere oxidizes copper very rapidly when in contact with solvents of the oxide of copper; and in this manner the metal becomes **oxidized and dissolved** in hydrochloric acid and nearly all acids, in ammonium hydroxide, in solutions of many salts, in fats, sugars, and other organic substances.

Copper forms **two oxides**, and corresponding series of salts: *cuprous salts* being infrequent and instable compounds, nearly all insoluble in water, and easily resolved into metallic copper and *cupric salts*, the stable and representative compounds of the metal.

Cupric salts are readily **reduced to cuprous** combinations by most strong reducing agents acting *with alkalis*, as, by sulphites (*a*) with free alkali (difficultly, without alkali); by arsenious acid, with excess of alkali; by glucose, and certain other sugars and organic materials, with excess of alkali. Also, by ferrous salts, in presence of iodides (345 *b*). Metallic iron

and zinc separate, from solutions of cupric salts, metallic copper, without formation of cuprous salt.



**337. CUPROUS oxide**— $\text{Cu}_2\text{O}$ —is of a brownish-red color; cuprous hydroxide— $\text{Cu}_2(\text{OH})_2$ —brownish-yellow. Cuprous salts are **insoluble** in water. The chloride,  $\text{Cu}_2\text{Cl}_2$ , dissolves in strong hydrochloric acid to a colorless solution, which turns green in the air.

*From this solution* water throws down the cuprous chloride, white; **fixed alkalis**, in small quantity, neutralize the free acid, and precipitate the white cuprous chloride; in larger quantity, precipitate the yellow cuprous hydroxide, insoluble in excess. **Ammonium hydroxide** and ammonium carbonate, in excess, redissolve the hydroxide, and dissolve the oxide to a colorless solution, which turns blue on exposure. Potassa precipitates the ammonia solution. Soluble **carbonates** precipitate the yellow cuprous carbonate,  $\text{Cu}_2\text{CO}_3$ .—**Iodide** of potassium precipitates the white cuprous iodide,  $\text{Cu}_2\text{I}_2$ , without liberation of iodine (345 b).—Hydrosulphuric acid and **sulphides** precipitate  $\text{Cu}_2\text{S}$ , black.—**Phosphates**, **oxalates**, **cyanides**, and **ferrocyanides** precipitate their respective cuprous salts, white; **ferricyanides**, brown-red. Ammoniacal solution of silver nitrate precipitates metallic silver.—With the **blow-pipe**, cuprous salts behave like cuprous compounds (349).

**338. Reactions of Cupric Salts.**—Cupric salts, in crystals or solution, have a green or blue color; the chloride (2 aq.) in solution is emerald-green when concentrated, light blue when dilute; the sulphate (5 aq.) is “blue vitriol.” Anhydrous cupric salts are white. The crystallized chloride is **deliquescent**; the sulphate, permanent; the acetate, efflorescent.

Cupric hydroxide, basic carbonate, oxalate, phosphate, borate, arsenite, sulphide, cyanide, ferrocyanide, ferricyanide, and tartrate are **insoluble** in water. The ammonio-oxide and most of the ammonio salts, the potassio and sodio cyanides, and the potassio and sodio tartrate, are soluble in water. In alcohol the sulphate and acetate are insoluble; the chloride and nitrate, soluble. Ether dissolves the chloride.

Copper is easily **identified** by reduction with iron to the lustrous metallic state (350); also, by the blue solution with excess of ammonium hydroxide (340), used as a separation from bismuth.

**339. Fixed alkalis**—**KOH**—added to saturation in solutions of copper salts, precipitate copper *hydroxide*,  $\text{Cu}(\text{OH})_2$ , deep blue, insoluble in excess, soluble in ammonium hydroxide (if too much fixed alkali is not present), very soluble in acids, and changed, by standing, to the black, basic hydrate,  $\text{Cu}_3\text{O}_2(\text{OH})_2$ ; by boiling, to  $\text{CuO}$ . If tartaric acid, citric acid, grape-sugar, milk-sugar, or certain other **organic** substances are present, the precipitate either does not form at all, or redissolves in excess of the fixed alkali to a blue solution. The tartrate alkaline solution may be boiled without change; in presence of sugar, the application of heat precipitates the yellow cuprous hydrate (346). The addition of alkali

hydroxides, *short of saturation*, forms insoluble basic salts, of a lighter blue than the hydrate.

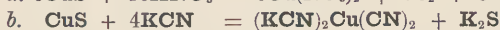
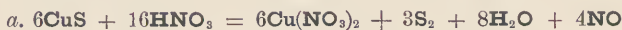
**340. Ammonium hydrate**, added short of saturation, precipitates the pale blue basic salts; added just to saturation, the deep blue hydroxide (in both cases *like the fixed alkalis*); added to supersaturation, the precipitate dissolves to an intensely deep blue solution. The blue solution consists of compounds of cuprammonium,  $(\text{N}_2\text{H}_6\text{Cu})''$ , a diammonium formed by the substitution of an atom of copper for an atom of hydrogen in each of two semi-molecules of ammonium,  $\text{NH}_3\text{NH}_3\text{Cu}$ . The cuprammonium oxide is united with ammonium salt, as  $(\text{N}_2\text{H}_6\text{Cu})\text{O} \cdot (\text{NH}_4)_2\text{SO}_4$  and  $(\text{N}_2\text{H}_6\text{Cu})\text{O} \cdot (\text{NH}_4\text{Cl})_2$ :



From this solution the fixed alkalis in strong solution precipitate the blue hydroxide, and on boiling the black oxide,  $\text{CuO}$ .

**341. Ammonium carbonate**, like ammonium hydroxide, precipitates and redissolves to a blue solution. **Carbonates** of fixed alkali metals—as  $\text{K}_2\text{CO}_3$ —precipitate the greenish-blue, basic carbonate,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ , of variable composition, according to conditions, and converted by boiling to the black, basic hydroxide and finally to the black oxide. Barium carbonate precipitates completely, on boiling, a basic carbonate.

**342. Hydrosulphuric acid**, and soluble **sulphides**, precipitate *copper sulphide*,  $\text{CuS}$ , black, formed alike in acid solutions (distinction from iron, manganese, cobalt, nickel) and in alkaline solutions (distinction from arsenic, antimony, tin).—Solutions containing only the one-hundred-thousandth of copper salt are colored brownish by the reagent. The precipitate,  $\text{CuS}$ , is easily soluble by nitric acid (*a*) (distinction from mercuric sulphide); with difficulty soluble by strong hydrochloric acid (distinction from antimony); insoluble in hot dilute sulphuric acid (distinction from cadmium); insoluble in fixed alkali sulphides, and but slightly soluble in ammonium sulphide (distinction from arsenic, antimony, tin); soluble in solution of potassium cyanide (*b*) (distinction from lead, bismuth, cadmium, mercury); soluble in solution of potassium carbonate.



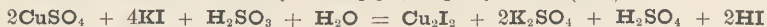
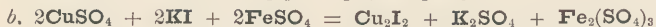
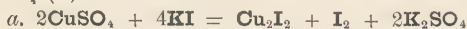
**343. Phosphates**—as  $\text{Na}_2\text{HPO}_4$ —give a bluish-white precipitate of *copper phosphates*;  $\text{CuHPO}_4$ , if the reagent is in excess;  $\text{Cu}_3(\text{PO}_4)_2$ , if the copper salt is in excess; the precipitates slightly soluble by acetic acid.—**Oxalates** precipitate *cupric oxalate*,  $\text{CuC}_2\text{O}_4$ , bluish-white, insoluble in acetic acid, and formed from mineral acid salts of copper by oxalic acid added with alkali acetates.—Normal potassium **chromate** precipitates brown-red basic cupric chromate, somewhat soluble in water.—**Arsenites**, as  $\text{K}_3\text{AsO}_3$ , or arsenious acid with just sufficient alkali hydroxide to neutralize it, precipitate from solutions of cupric salts (not the acetate) the green *copper*.

*arsenite*, chiefly  $\text{CuHAsO}_3$  (Schcele's green, "Paris green"), readily soluble in acids and in ammonium hydroxide, decomposed by strong potassium hydroxide solution. From cupric *acetate*, arsenites precipitate, on boiling, *copper aceto-arsenite*,  $(\text{CuOAs}_2\text{O}_3)_3\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ , Schweinfurt green or Imperial green, "Paris green," dissolved by ammonium hydroxide and by acids, decomposed by fixed alkalis.

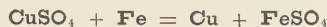
**344. Alkaline cyanides**—as  $\text{KCN}$ —precipitate at first the yellowish-green *cyanide*,  $\text{Cu}(\text{CN})_2$ , soluble in excess of the reagent by formation of potassium cupric cyanide,  $\text{K}_2\text{Cu}(\text{CN})_4$ . The cupric cyanide precipitate is instable, becoming cuprous, or cuproso-cupric cyanide,  $\text{Cu}_2(\text{CN})_3$ ; the latter unites with ammonium hydroxide, forming several green to blue salts, mostly soluble in water. **Ferrocyanides**—as  $\text{K}_4\text{Fe}(\text{CN})_6$ —precipitate the *copper ferrocyanide*,  $\text{Cu}_2\text{Fe}(\text{CN})_6$ , reddish-brown, insoluble by acids, decomposed by alkalis. In highly dilute solutions a reddish coloration, without precipitate, is seen. **Ferricyanides**—as  $\text{K}_3\text{Fe}_2(\text{CN})_{12}$ —precipitate *copper ferricyanide*,  $\text{Cu}_3\text{Fe}_2(\text{CN})_{12}$ , yellowish-green, insoluble in hydrochloric acid. **Thiocyanates**, with sulphurous or hypophosphorous acid, precipitate *cuprous thiocyanate*,  $\text{Cu}_2(\text{CNS})_2$ , white (distinction from cadmium).

**345. Soluble iodides** precipitate, from concentrated solutions of *copper* salts, *cuprous iodide*,  $\text{Cu}_2\text{I}_2$ , white, colored dark brown by the *iodine* separated in the reaction (a). The iodine dissolves with color in excess of the reagent, or dissolves colorless on adding ferrous sulphate or soluble sulphites, by entering into combination. Cuprous iodide dissolves in thiosulphates (with combination).

The cuprous iodide is precipitated, free from iodine, and more completely, by adding *reducing agents* with iodides; as,  $\text{Na}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{FeSO}_4$  (b).



**346. Metallic copper** is reduced and separated from cupric solutions by *iron*, *zinc*, cobalt, nickel, lead, cadmium, bismuth, tin, and phosphorus. A bright slip of iron in solution of cupric salts acidulated with hydrochloric acid, receives a bright copper coating, recognizable from solutions in 120,000 parts of water. Zinc acts most promptly in contact with platinum, as by use of a platinum dish, when the copper is deposited on the platinum; when minutely divided as a precipitate, the copper is dark brown to black. Finely divided zinc can be removed by solution in hydrochloric acid. Nitric acid and tartaric acid interfere with this reaction:



(For every 63 parts of copper deposited, 55.9 parts of iron are dissolved.)

For detection of minute *traces* of copper, by metallic reduction, Hager directs as follows: The material is obtained in solution acidulated with acetic acid. The end of a



platinum wire is inserted just within the eye of a large sewing-needle, around which the wire is wound. The coil is left in the solution three or four hours, at a temperature of  $25^{\circ}$  to  $30^{\circ}$  C. ( $77^{\circ}$  to  $86^{\circ}$  F.) The presence of copper is indicated by a black-brown coating on the platinum wire, but more closely determined by further treatment. The needle is now withdrawn, the platinum wire is washed by gentle introduction into water, placed in a test tube, treated with four or five drops of nitric acid and a few drops of diluted sulphuric acid, warmed, boiled to expel all nitric acid, and an excess of ammonium hydroxide added.

**Hydrobromic Acid.**—To one drop of the copper solution add two drops of **HBr**, and concentrate by evaporation to one-half of its volume; the rose-red color indicates copper. 0.01 of a milligramme of copper may thus be detected. Of the common metals only iron interferes. **KBr** and **H<sub>2</sub>SO<sub>4</sub>** may be substituted for the **HBr**.

**Arsenious acid**, certain sugars, and many organic compounds, reduce cupric salts with fixed alkali hydroxide to a yellow precipitate of *cuprous oxide* and not to metallic copper.

**Sodium thiosulphate**, **Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>**, added to hot solutions of copper salts, gives a black precipitate. In solutions strongly acidulated (with hydrochloric acid) this is a separation from cadmium.

**347. Ignition** with sodium carbonate on charcoal leaves metallic copper in finely divided grains. The particles are gathered by triturating the charcoal mass in a small mortar, with the repeated addition and decantation of water until the copper subsides clean. It is recognized by its color, and its softness under the knife.

**348.** Copper readily dissolves, from its compounds in **beads** of borax and of microcosmic salt, in the outer flame of the blow-pipe. The beads are green while hot, and *blue* when cold. In the inner flame the borax bead becomes colorless when hot; the microcosmic salt turns dark green when hot, both having a reddish-brown tint when cold (**Cu<sub>2</sub>O**) (helped by adding tin).

**349.** Compounds of copper, heated in the inner flame, **color the outer flame green**. Addition of hydrochloric acid increases the delicacy of the reaction, giving a greenish-blue color to the flame.

**350. Estimation.**—(1) It is precipitated by means of zinc in a platinum dish (or a small battery may be employed) and weighed as metallic copper. Or it may be converted into **CuH<sub>2</sub>** by treating with **H<sub>3</sub>PO<sub>2</sub>**, and after reducing to metallic copper by ignition weighed as such. (2) It is converted into **CuO** and weighed after ignition. (3) It may be precipitated either by **H<sub>2</sub>S** or **Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>**, and, after adding free sulphur and igniting in hydrogen gas, weighed as cuprous sulphide, or it may be precipitated by **KCN**S in presence of **H<sub>2</sub>SO<sub>4</sub>**, or **H<sub>3</sub>PO<sub>2</sub>**, and, after adding **S**, ignited in **H** and weighed as **Cu<sub>2</sub>S**. **Cu<sub>2</sub>O**, **CuO**, **Cu(NO<sub>3</sub>)<sub>2</sub>**, **CuCO<sub>3</sub>**, **CuSO<sub>4</sub>**, and many other cupric salts, are converted



into  $\text{Cu}_2\text{S}$  by adding **S** and igniting in hydrogen gas. (4) By adding **KI** to the cupric salt and titrating the liberated **I** by  $\text{Na}_2\text{S}_2\text{O}_3$ ; not permissible with acid radicals which oxidize **HI**. (5) By precipitating as **Cu**, dissolving in  $\text{Fe}_2\text{Cl}_6$ ,



and titrating the latter by  $\text{K}_2\text{Mn}_2\text{O}_8$ . (6) By reducing with a solution of  $\text{SnCl}_2$  of known strength in presence of free **HCl**



the end of the reaction is known by the disappearance of the green color of  $\text{CuCl}_2$ .

**351. Oxidation.**—Solutions of  $\text{Cu}''$  and  $(\text{Cu}_2)''$  are reduced to the metallic state by **Zn**, **Cd**, **Sn**, **Al**, **Pb**, **Fe**, **Co**, **Ni**, **Bi**, and in presence of **KOH** by  $\text{K}_2\text{SnO}_3$ .  $\text{Cu}''$  is reduced to  $(\text{Cu}_2)''$  by  $\text{SnCl}_2$  in presence of **HCl**, and in presence of **KOH** by  $\text{As}_4\text{O}_6$  and by grape sugar. Metallic copper is oxidized to  $\text{Cu}''$  by solutions of  $\text{Hg}''$ ,  $(\text{Hg}_2)''$ ,  $\text{Ag}'$ ,  $\text{Pt}^{\text{IV}}$ , and  $\text{Au}'''$ , these salts being reduced to the metallic state. Copper is also oxidized by many acids.

#### BISMUTH. $\text{Bi} = 207.523$ .

**352. Specific gravity**, 9.759 (SCHRÖDER, 1859). *Melting point*,  $268.3^\circ \text{C}$ . ( $515^\circ \text{F}$ .) (RIEMSDYK, 1869). Valence, a triad in  $\text{Bi}''' \text{Cl}_3$ , a pentad in  $\text{Bi}_2\text{O}_5$ , and in  $\text{Bi}_2\text{O}_3$  a dyad.

**353. Occurrence.**—A comparatively rare metal, usually found native; also found as bismuth ochre ( $\text{Bi}_2\text{O}_3$ ), bismuthite or bismuth glance ( $\text{Bi}_2\text{S}_3$ ), and in some other minerals.

**354. Preparation.**—On a large scale it is always reduced from its ores by fusing with carbon. It may also be produced by fusing with **K**, **Na**, **CO**, **KCN**,  $\text{H}_2\text{C}_2\text{O}_4$ , or  $\text{NH}_4\text{Cl}$ .

**355. Properties.**—A hard, brittle, reddish-white metal. Its melting point is lowered by alloying with other metals. *Fusible metal* consists of, in parts by weight, 2 **Bi**, 1 **Sn**, 1 **Pb**, and melts at  $93.7^\circ \text{C}$ ., "*Wood's Metal*," 15 **Bi**, 8 **Pb**, 4 **Sn**, 3 **Cd**, melts at  $68^\circ \text{C}$ . Bismuth may be distilled in an atmosphere of **H** above  $1100^\circ \text{C}$ .

**356. Oxides.**—Four oxides are known— $\text{Bi}_2\text{O}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_4$ ,  $\text{Bi}_2\text{O}_5$ . Dibismuth dioxide ( $\text{Bi}_2\text{O}_2$ ) is sometimes called *hypobismuthous oxide* (*Watts' Dictionary*, 1888); and more properly *bismuthous oxide* (*Graham Otto's Chemie*, 1888). It is formed by the action of potassium stannite upon bismuth hydroxide—



A black powder easily oxidized to  $\text{Bi}'''$ . A corresponding dibismuth tetrachloride,  $\text{Bi}_2\text{Cl}_4$ , is formed when metallic bismuth is heated with  $\text{BiCl}_3$ ,  $\text{Hg}_2\text{Cl}_2$ , or **Cl** in the right proportions. It is instable. Bismuth peroxide,  $\text{Bi}_2\text{O}_5$ , is formed when **Cl** is passed into a hot solution of **KOH**, containing

$\text{Bi}(\text{OH})_3$ . It is a reddish powder. Non-reducing acids, such as  $\text{H}_2\text{SO}_4$ , change it to  $\text{Bi}'''$ , with evolution of oxygen. Reducing acids are themselves oxidized, no oxygen being given off—*e.g.*,



Dibismuth tetroxide, ( $\text{Bi}_2\text{O}_4$ ), is little known; formed like  $\text{Bi}_2\text{O}_3$ , but using less chlorine. It *may* be considered in its valence as a union of  $\text{Bi}'''$  and  $\text{Bi}^v$ ,  $2\text{Bi}_2\text{O}_4 = \text{Bi}_2\text{O}_3 + \text{Bi}_2\text{O}_5$ .

**Bismuth oxide** and its corresponding salts are stable. It has a yellowish-white color ( $\text{Bi}(\text{OH})_3$  is white); is formed when any other bismuth oxides, hydroxides, organic salts, or inorganic oxysalts with volatile acids, are ignited in the air. Bismuth hydroxide,  $\text{Bi}(\text{OH})_3$ , is formed by precipitating bismuth salts with alkalis.

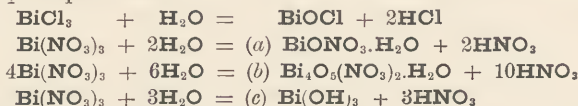
**357. Solubilities.**—Bismuth is but slightly **oxidized** in the air at ordinary temperatures, rapidly at a red heat; it takes fire in chlorine, and unites readily with bromine, iodine, and sulphur. Hydrochloric acid scarcely attacks it; boiling sulphuric acid salifies it with separation of sulphurous anhydride, but it **dissolves** much the most readily in nitric acid, with evolution of lower oxides of nitrogen.

The sulphide, hydroxide, basic carbonate, phosphate, chromate, borate, sulphite, oxalate, iodide (364), cyanide, ferrocyanide, ferricyanide, tartrate, citrate, tannate, and valerianate are **insoluble** in water. The chloride, bromide (364), nitrate, chlorate, and sulphate—when taken as normal salts—are soluble in water acidulated with their respective acids, or with other acids forming “soluble” bismuth salts; but are decomposed by pure water, with partial solution and partial separation of insoluble *basic* salts—(326 and equations in 358). The ammonio citrate is soluble in water without decomposition; and the decomposition of the normal chloride, nitrate, and sulphate is prevented by the addition of comparatively small quantities of acetic, citric, and certain other organic acids. The acidulated, water-saturated solutions of the nitrate and chloride may be considerably further diluted with alcohol, without disturbance.

In **analysis**, bismuth is precipitated alone, from the nitric acid solution of second-group sulphides, after removing lead (and silver), by adding excess of ammonium hydroxide, a separation from copper and cadmium. The precipitation by water (358) suggests bismuth.

**358. Water** precipitates, from the acidulated bismuth solutions, white *basic salts* (see equations below), which contain less of their acid radicals in proportion as greater quantities of water are added, and some of which can be washed on the filter until almost pure hydroxide or oxide. The precipitation is most complete with the chloride, and with other salts is promoted by addition of hydrochloric acid or **chlorides**; hence it may occur as a first-group precipitate. All the precipitates are readily soluble in hydrochloric and nitric acids; not in tartaric acid (distinction from antimony). Acidu-

lation with certain organic acids (in accordance with the statement in 357) prevents the precipitation :



359. The **alkali hydroxides** precipitate from bismuth solutions—in absence of tartaric acid, citric acid, and certain other organic substances—the white *bismuth hydroxide*,  $\text{Bi}(\text{OH})_3$ , insoluble in excess of the reagents, converted by boiling to the oxide,  $\text{Bi}_2\text{O}_3$ , yellowish-white. Certain reducing agents turn the precipitate black (366).

360. The **carbonates** precipitate *basic bismuth carbonate*,  $\text{Bi}_2\text{O}_2\text{CO}_3$ , white, insoluble in excess. Barium carbonate forms the same precipitate, without heating.

361. **Hydrosulphuric acid** and **sulphides** precipitate *bismuth sulphide*,  $\text{Bi}_2\text{S}_3$ , black, insoluble in dilute acids and in alkali hydroxides; insoluble in alkali sulphides (distinction from arsenic, tin, antimony), and in alkali cyanides (distinction from copper). It is soluble by moderately concentrated nitric acid (distinction from mercury), the sulphur mostly remaining free.

362. Soluble **chromates**—both  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ —precipitate the yellow, basic *bismuth chromate*,  $\text{Bi}_2\text{O}(\text{CrO}_4)_2$ , distinguished from that of lead by its insolubility in fixed alkali hydroxide.

363. Phosphoric acid and soluble **phosphates** precipitate *bismuth phosphate*,  $\text{BiPO}_4$ , insoluble in five per cent. nitric acid, insoluble in dilute acetic acid, readily soluble in hydrochloric and sulphuric acids.—Arsenic acid and **arseniates** form a precipitate corresponding to the phosphate in composition, and having the same solubilities.

364. Oxalic acid and **oxalates** precipitate *bismuth oxalate*,  $\text{Bi}_2(\text{C}_2\text{O}_4)_3$ , white, insoluble in dilute acids.

**Potassium Iodide** produces in slightly acidulated solutions of bismuth salts—not acidulated to excess with hydrochloric acid—a dark brown precipitate of *bismuth iodide*, partly basic, soluble in excess of the reagent, in hydrochloric acid and in hydriodic acid—in each case with a brown tinge to the solution, not soluble in dilute nitric acid.\*

**Bromides** precipitate a basic salt, soluble in acid.

\* This precipitate, at the moment of its formation in concentrated solutions, is doubtless normal bismuth iodide,  $\text{BiI}_3$ , which is gradually decomposed by water, more rapidly in dilute solutions, forming basic iodide (oxy-iodide) with separation of hydriodic acid. The oxy-iodide of the composition  $\text{BiOI}$  is stated to be insoluble in solutions of alkali iodides, while this precipitate is soluble in these solutions, even after decomposition by much water.

The reaction of iodides, with bismuth solutions, differs in degree but not in kind from that of chlorides; the normal bismuth iodide only requiring stronger acidulation to hold it in solution than the normal chloride. Also, intermediate between the behavior of these two lies that of bismuth bromide. The aqueous iodides form a very delicate test for even quite strongly acidulated solutions of bismuth salts, and the bismuth iodide may not improperly be classed as an "insoluble" salt (357).

**365.** Alkaline cyanides precipitate the white *hydroxide*  $\text{Bi}(\text{OH})_3$ , with formation of hydrocyanic acid. The precipitate is insoluble in the reagent. —**Ferrocyanides** form a white to yellow precipitate; **ferri-cyanides** a yellow to brownish-yellow precipitate—both normal bismuth salts, and both insoluble in acids.

**Tannic acid** throws down bismuth tannate, yellow.

**366.** *Metallic bismuth* is **reduced** from bismuth solutions, mostly as a spongy precipitate, by **zinc, iron, tin, lead, copper, and cadmium.**

**Potassium or sodium stannite** ( $\text{K}_2\text{SnO}_3$ ), when added in excess to bismuth solutions, causes a black precipitate, from reduction to *dibismuth dioxide*,  $\text{Bi}_2\text{O}_3$ , a very delicate reaction. The stannite is made, when wanted, by adding to stannous chloride solution, in a test-tube, enough sodium or potassium hydroxide to redissolve the precipitate at first formed.

The basic bismuth nitrate is reduced by **grape sugar**, in a warm solution of fixed alkali carbonate with formation of a blackish-brown liquid and dark-gray sediment containing *dibismuth dioxide*. Also, the recent bismuth hydroxide, in suspension with the excess of fixed alkali, is reduced by digestion with grape sugar or milk sugar to a black precipitate.

**367.** On charcoal, with sodium carbonate, before the **blow-pipe**, bismuth is readily reduced from all its compounds. The *globule* is easily fusible, brittle (distinction from lead), and gradually oxidizable under the flame, forming an *incrustation* ( $\text{Bi}_2\text{O}_3$ ), orange-yellow while hot, lemon-yellow when cold, the edges bluish-white when cold. The incrustation disappears, or is driven by the reducing flame, without giving color to the outer flame.

With borax or microcosmic salt, bismuth gives **beads**, faintly yellowish when hot, colorless when cold.

**368. Estimation.**—(1) As metallic bismuth formed by fusion with potassium cyanide. (2) As  $\text{Bi}_2\text{O}_3$  formed by ignition of bismuth salts of organic acids, or of the salts of volatile inorganic oxyacids. (3) By precipitation by  $\text{H}_2\text{S}$ , and after drying at  $100^\circ \text{C}$ ., weighing as  $\text{Bi}_2\text{S}_3$ . (4) By precipitation by  $\text{K}_2\text{Cr}_2\text{O}_7$ , and after drying at  $120^\circ \text{C}$ ., weighing as  $\text{Bi}_2\text{O}(\text{CrO}_4)_2$ .

**369. Oxidation.**—All compounds of bismuth having less than five bonds are oxidized to  $\text{Bi}^{\text{v}}$  by **Cl**, in presence of **KOH**. The *triad* is reduced to the *dyad* in presence of **KOH** by  $\text{K}_2\text{SnO}_3$ , and by grape sugar. Metallic bismuth reduces salts of **Hg, Ag, Pt, and Au** to the metallic state. From bismuth salts the free metal is precipitated by **Zn, Mg, Al, Cd, Pb, Fe, and Cu.**



CADMIUM.  $\text{Cd} = 111.835$ .

**370. Specific gravity**, hammered, 8.667 (SCHRÖDER, 1859). *Vapor density* ( $\text{H} = 1$ ), 55.8 (DEVILLE and TROOST, 1861). *Melting point*,  $320^\circ \text{C}$ . ( $608^\circ \text{F}$ .) (RIEMSDYK, 1869). *Boiling point*,  $763^\circ$  to  $772^\circ \text{C}$ . (CARNELLEY and WILLIAMS, 1878).

**371. Occurrence**.—Found in greenockite ( $\text{CdS}$ ), and with zinc in many of its ores.

**Preparation**.—Reduced by carbon and separated from zinc (approximately) by distillation, the cadmium being more volatile. It may be reduced by fusion with  $\text{H}$ ,  $\text{CO}$ , or coal gas.

**372. Properties**.—A white crystalline metal, soft, but harder than tin or zinc; more tenacious than tin; malleable and very ductile, can easily be rolled out into foil or drawn into fine wire, but at  $80^\circ \text{C}$ . it is brittle. It may be completely distilled in a current of hydrogen above  $800^\circ \text{C}$ .; only slightly tarnished by air and water at ordinary temperatures. When ignited burns to  $\text{CdO}$ . When heated combines directly with  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{S}$ ,  $\text{Se}$ ,  $\text{P}$ , and  $\text{Te}$ . It forms many useful alloys.

**Oxide and Hydroxide**.—Its only hydroxide,  $\text{Cd}(\text{OH})_2$ , is formed from its salts by precipitation with  $\text{KOH}$  or  $\text{NaOH}$ ; and its only oxide ( $\text{CdO}$ ), by ignition of  $\text{Cd}(\text{OH})_2$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{CdC}_2\text{O}_4$ ,  $\text{CdCO}_3$ , etc.

**373. Solubilities**.—It dissolves slowly in hot, moderately dilute hydrochloric or sulphuric acid, with evolution of hydrogen; in nitric acid, more readily with generation of nitrogen oxides.—Cadmium forms a single oxide,  $\text{Cd}''\text{O}$ , yellowish-brown, and a corresponding series of salts, from which it is reducible, in the wet way, only by strong reducing agents. It forms numerous double salts, especially haloids.—The hydroxide, sulphide, carbonate, oxalate, phosphate, cyanide, ferrocyanide, and ferricyanide are **insoluble** in water. The chloride and bromide are **deliquescent**, and soluble in alcohol as well as water; the iodide is permanent, and soluble in water and alcohol; very sparingly in ether. The ammonio-oxide and the potassio and sodio cyanides are soluble in water.

All of its salts that are insoluble in water are soluble in hydrochloric and nitric acids and in ammonium hydroxide, except  $\text{CdS}$ .

**374. Reactions of Cadmium Salts**.—Fixed **alkalies** precipitate from solutions of cadmium salts—in absence of tartaric and citric acids, and certain other organic substances—the white *hydroxide*,  $\text{Cd}(\text{OH})_2$ , insoluble in excess of the reagents (distinction from zinc). Ammonium hydroxide forms the same precipitate, which it redissolves. Alkali **carbonates** precipitate  $\text{CdCO}_3$ , white, insoluble in excess of the reagents. Barium carbonate forms a complete precipitate, in the cold.—**Hydrosulphuric acid** and sulphides throw down the *sulphide*,  $\text{CdS}$ , yellow; insoluble in cold dilute acids, in alkalies, and in alkali sulphides and cyanides, soluble in hot and dilute sulphuric acid (compare 375).—Alkali **chromates** precipitate yellow *cadmium chromate*, from concentrated solutions only, and soluble on addition of water.—**Phosphates** form a white precipitate, readily soluble in acids; **oxalates** and oxalic acid, cadmium oxalate, white, difficultly soluble in acids. Potassic **cyanide** precipitates  $\text{Cd}(\text{CN})_2$ , white; soluble in excess of the reagent, as  $\text{K}_2\text{Cd}(\text{CN})_4$ ; ferrocyanides form a white; ferricyanides, a yellow precipitate—both soluble in hydrochloric acid, and in ammonium hydroxide.

On charcoal, with sodium carbonate, cadmium is reduced before the



**blow-pipe** to metallic salt, and usually vaporized and reoxidized nearly as fast as reduced, thereby forming a characteristic brown incrustation ( $\text{CdO}$ ). This is volatile by reduction only, being driven with the reducing flame.—Cadmium oxide colors the borax **bead** yellowish while hot, colorless when cold; microcosmic salt, the same.

**375.** *Cadmium may be separated from copper:* (1) By the solubility of  $\text{CuS}$  in  $\text{KCN}$ ,  $\text{CdS}$  being insoluble in  $\text{KCN}$ ; or, better, by treating the blue ammoniacal solution with  $\text{KCN}$  until the blue color disappears, then  $\text{H}_2\text{S}$  will precipitate the cadmium as  $\text{CdS}$ , while the copper remains in solution. (2) By reduction of the copper to  $\text{Cu}_2\text{Cl}_2$  with  $\text{SnCl}_2$  and its precipitation with milk of sulphur, removal of excess of tin with  $\text{NH}_4\text{OH}$  and precipitation of the cadmium with  $\text{H}_2\text{S}$ . (3) The solution is acidified with  $\text{HCl}$  and the copper precipitated with hot  $\text{Na}_2\text{S}_2\text{O}_3$ , and the cadmium in the filtrate is precipitated by  $(\text{NH}_4)_2\text{S}$  after neutralization with  $\text{NH}_4\text{OH}$ . (4) From the mixed sulphides,  $\text{CdS}$  is dissolved by dilute hot  $\text{H}_2\text{SO}_4$  (one part  $\text{H}_2\text{SO}_4$  to five of  $\text{H}_2\text{O}$ ).

### 376. Comparison of Certain Reactions of Bismuth, Copper, and Cadmium.

*Taken in Solutions of their Chlorides, Nitrates, Sulphates, or Acetates.*

	Bi.	Cu.	Cd.
<b>KOH</b> or <b>NaOH</b> , in excess.	$\text{Bi}(\text{OH})_3$ , white.	$\text{Cu}(\text{OH})_2$ , dark blue.	$\text{Cd}(\text{OH})_2$ , white.
<b><math>\text{NH}_4\text{OH}</math></b> , in excess.	$\text{Bi}(\text{OH})_3$ , white.	Blue solution.	Colorless solution.
<b>Dilution</b> of saturated solutions.	$\text{BiOCl}$ , etc., white.		
<b>Iodides.</b>	Partial precip., in solutions not very strongly acid (364).	Partial precipitate completed by reducing agents (345).	No pre.
<b>Sulphides.</b>	$\text{Bi}_2\text{S}_3$ , black, insol. in cyanide.	$\text{CuS}$ , black, sol. in cyanide (375).	$\text{CdS}$ , yellow, insoluble in cyanide.
<b>Iron</b> or <b>Zinc.</b>	$\text{B}^*$ (spongy precip.) (378).	$\text{Cu}$ (bright coating) (351).	$\text{Cd}$ (gray sponge).
<b>Sugar</b> , <b>KOH</b> and heat.	$\text{BiO}$ and $\text{Bi}$ (black) (366).	$\text{Cu}_2(\text{OH})_2$ (yellow).	
<b><math>\text{K}_2\text{SnO}_2</math></b> + <b>KOH.</b>	$\text{Bi}_2\text{O}_3$ (black).	Metallic copper.	Metallic cadmium.

**377. Estimation.**—(1) It is converted into, and after ignition weighed as, an oxide; (2) converted into, and after drying at  $100^\circ\text{C}$ ., weighed as  $\text{CdS}$ ; (3) precipitated as

$\text{CdC}_2\text{O}_4$  and titrated by  $\text{K}_2\text{Mn}_2\text{O}_8$ ; (4) precipitated as  $\text{CdS}$  and reduced with  $\text{Fe}_2\text{Cl}_6$ , and the amount of reduction determined by  $\text{K}_2\text{Mn}_2\text{O}_8$ .

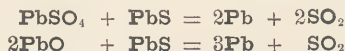
**378. Oxidation.**—Metallic cadmium precipitates the free metals from solutions of **Au**, **Pt**, **Ag**, **Hg**, **Bi**, **Cu**, **Pb**, **Sn**, and **Co**; and is itself reduced by **Zn**, **Mg**, and **Al**.

### LEAD. $\text{Pb} = 206.471$ .

**379. Specific gravity**, 11.38 (REICH). *Melting point*,  $326.2^\circ \text{C}$ . ( $619.2^\circ \text{F}$ ) (PERSON, 1849). Valence, a dyad in  $\text{Pb}^{\text{II}}\text{O}$ , and in all lead salts; a tetrad, in  $\text{Pb}^{\text{IV}}\text{O}_2$  and in plumbates.

**380. Occurrence.**—Lead is seldom found in the free state in nature. Its chief ore is galena ( $\text{PbS}$ ). In smaller quantities it is found as cerussite, or white lead ore ( $\text{PbCO}_3$ ); as anglesite ( $\text{PbSO}_4$ ), and in very many other minerals.

**381. Preparation.**—From galena (1) It is roasted in the air, forming variable quantities of  $\text{PbSO}_4$ ,  $\text{PbO}$ , and  $\text{PbS}$ ; then the air is excluded and the temperature raised, and the sulphur of the sulphide reduces both the  $\text{PbO}$  and the  $\text{PbSO}_4$ ,  $\text{SO}_2$  being formed:



(2) Similar to the first except that some form of carbon is used to aid in the reduction. (3) It is reduced by fusing with metallic iron ( $\text{PbS} + \text{Fe} = \text{Pb} + \text{FeS}$ ). Frequently these methods are combined or varied according to the other ingredients of the ore.

**382. Properties**—A bluish-white, soft metal; it can be rolled out into sheets, but not drawn into wire; nearly inelastic; is a poor conductor of heat and electricity; it forms alloys with most metals. Solder is lead one part, tin one part; type metal, lead two parts, tin and antimony each one part. Shot contains 0.5 per cent. of arsenic. Lead is slowly volatile at a white heat. It tarnishes in the air at ordinary temperatures by formation of diplumbic monoxide,  $\text{Pb}_2\text{O}$ , blackish gray. Pure water, free from air, does not affect lead, free from oxide or hydroxide, in the cold; but granulated lead slowly decomposes boiling water, with evolution of hydrogen, and formation of lead hydroxide,  $\text{Pb}(\text{OH})_2$ . In water containing air, the hydroxide and basic carbonate are formed. This corrosion and solution are greatly promoted by nitrogenous organic matters—ammonium salts, and nitrates and nitrites—and by chlorides; hindered or prevented by carbonates, acid carbonates and sulphates. Above the melting point, lead gradually oxidizes in the air to "litharge,"  $\text{PbO}$ .

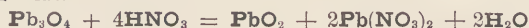
**383. Oxides.**—Lead forms four oxides,  $\text{Pb}_2\text{O}$ ,  $\text{PbO}$ ,  $\text{PbO}_2$ , and  $\text{Pb}_3\text{O}_4$ . *Lead sub-oxide* ( $\text{Pb}_2\text{O}$ ) is little known; it is the black powder formed when  $\text{PbC}_2\text{O}_4$  is heated to  $300^\circ \text{C}$ ., air being excluded. *Lead oxide* (litharge, or massicot) is formed by intensely igniting in the air  $\text{Pb}$ ,  $\text{Pb}_2\text{O}$ ,  $\text{PbO}_2$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{Pb}(\text{OH})_2$ ,  $\text{PbCO}_3$ ,  $\text{PbC}_2\text{O}_4$ , or  $\text{Pb}(\text{NO}_3)_2$ . It has a yellowish-white color, melts at a red heat, and is volatile at a white heat.

**384. Triplumbic tetroxide** (red lead or minium),  $\text{Pb}_3\text{O}_4$ , is formed by heating  $\text{PbO}$  to a dull-red heat with full access of air for several hours. Strong, non-reducing acids, such as  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_3$ , etc., convert it into a lead salt and  $\text{PbO}_2$  (a). But concentrated hot  $\text{H}_2\text{SO}_4$  converts the whole into  $\text{PbSO}_4$ , oxygen being evolved (b). But with the dilute acid and reducing agents, such as glycerine, sugar,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ , **Zn**, **Al**, **Cd**, **Mg**, **As**, **Pb**, etc., it is all reduced to the *dyad lead* without evolution of oxygen (c), (d), and (e). Hydracids usually reduce the lead and are themselves oxidized (f).

- (a)  $\text{Pb}_3\text{O}_4 + 2\text{H}_2\text{SO}_4$  (dilute) =  $\text{PbO}_2 + 2\text{PbSO}_4 + 2\text{H}_2\text{O}$   
 (b)  $2\text{Pb}_3\text{O}_4 + 6\text{H}_2\text{SO}_4$  (concentrated and hot) =  $6\text{PbSO}_4 + 6\text{H}_2\text{O} + \text{O}_2$   
 (c)  $\text{Pb}_3\text{O}_4 + \text{H}_2\text{C}_2\text{O}_4 + 6\text{HNO}_3 = 3(\text{Pb}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{CO}_2$   
 (d)  $10\text{Pb}_3\text{O}_4 + \text{As}_4 + 30\text{H}_2\text{SO}_4 = 30\text{PbSO}_4 + 4\text{H}_3\text{AsO}_4 + 24\text{H}_2\text{O}$   
 (e)  $\text{Pb}_3\text{O}_4 + \text{Zn} + 4\text{H}_2\text{SO}_4 = 3\text{PbSO}_4 + \text{ZnSO}_4 + 4\text{H}_2\text{O}$   
 (f)  $\text{Pb}_3\text{O}_4 + 8\text{HCl} = 3\text{PbCl}_2 + \text{Cl}_2 + 4\text{H}_2\text{O}$

The *valence* of  $\text{Pb}_3\text{O}_4$  is best explained by the theory that it is a union of the dyad and tetrad ( $\text{Pb}''$  and  $\text{Pb}^{\text{IV}}$ ),  $\text{Pb}_3\text{O}_4 = 2\text{Pb}''\text{O} + \text{Pb}^{\text{IV}}\text{O}_2$ .

**385. Lead dioxide or peroxide ( $\text{PbO}_2$ ),** is formed (1) by fusion of  $\text{PbO}$  with  $\text{KClO}_3$  or  $\text{KNO}_3$ ; (2) by fusing  $\text{Pb}_3\text{O}_4$  with  $\text{KOH}$ ; (3) by treating any compound of  $\text{Pb}''$  with  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{K}_6\text{Fe}_2(\text{CN})_{12}$ ,  $\text{K}_2\text{Mn}_2\text{O}_8$ , or  $\text{H}_2\text{O}_2$  in presence of  $\text{KOH}$ ; (4) by treating  $\text{Pb}_3\text{O}_4$  with non-reducing acids.



Ignition forms first  $\text{Pb}_3\text{O}_4$  and above a red heat  $\text{PbO}$ , oxygen being given off. It dissolves in acids on same conditions as  $\text{Pb}_3\text{O}_4$  (see 384). Very strong solution of potassium hydroxide, in large excess, dissolves it, with formation of "potassium plumbate,"  $\text{K}_2\text{PbO}_3$ . Lead dioxide is a powerful oxidizing agent, one of the strongest known. Digested with ammonium hydroxide, it forms lead nitrate and water. Triturated with one-sixth of sulphur, or tartaric acid, or sugar, it takes fire; with phosphorus, it detonates.

**386. Solubilities.**—Dilute nitric acid is the proper salifying solvent for metallic lead, forming plumbic nitrate with evolution of nitric oxide. Concentrated nitric acid acts more slowly. Lead does not dissolve in dilute sulphuric acid, cold or hot, or in concentrated sulphuric or hydrochloric acid, in the cold; but hot sulphuric acid, containing less than twenty-five per cent. water, forms lead sulphate, sparingly soluble in the concentrated acid; and hot concentrated hydrochloric acid forms, with evolution of hydrogen, and dissolves, a limited proportion of lead chloride. Dilute hydrochloric acid forms chloride, but dissolves little of it.

The oxide, and hydroxide (formed in water, 382), are soluble in 7,000 to 10,000 parts of water, to which they give the alkaline reaction. The sulphide, carbonate, phosphate, chromate, sulphite, borate, cyanide, ferrocyanide, and tannate are insoluble in water. The sulphate and oxalate are very slightly soluble in water; the chloride, iodide, bromide, and ferriocyanide are sparingly soluble in hot water, still more sparingly soluble in cold water. The sulphate and chloride are less soluble in dilute sulphuric and hydrochloric acids than in pure water, but much more soluble in the same acids concentrated than in water. Nitric acid increases the solubility of the sulphate and chloride in water, more and more, as the nitric acid is stronger—the salts separating again on diluting the nitric acid solution. The sulphate and chloride are insoluble in alcohol. The iodide is moderately soluble in solutions of alkaline iodides, insoluble in alcohol, decomposed by ether. The basic acetates are permanently soluble (if carbonic acid is strictly excluded). The basic nitrates are but slightly soluble in water, and are precipitated on adding solutions of potassium nitrate to solution of basic lead acetate.

In *analysis*, the solubility of the chloride, sparing as it is, enables lead to be separated from the other first-group metals. As a final precipitate, in both first and second groups, the sulphate is most used. The sulphide precipitate exceeds other tests in delicacy.

**387. Fixed alkalis** precipitate, from solutions of lead salts, *lead hydroxides*,  $\text{Pb}(\text{OH})_2$ , white, soluble in excess of the reagents, by combination, as potassium or sodium plumbite,  $\text{K}_2\text{PbO}_2$  (distinction from silver, mercury,

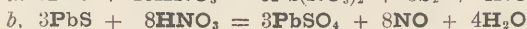
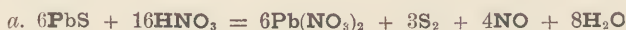
bismuth, copper, cadmium). *All the precipitates of lead hereafter given, except the sulphide and ferricyanide, are soluble in strong solutions of the fixed alkali hydroxides.*

The alkaline solution of lead is precipitated by alkaline solutions of chromic, stannic, stannous, antimonious, and arsenious oxides.

**Ammonium hydroxide** precipitates white basic salts, insoluble in excess (distinction from silver, copper, cadmium): with the chloride, the precipitate is  $\text{Pb}_2\text{OCl}_2$ ; with the nitrate,  $\text{Pb}_3\text{O}_2\text{OHNO}_3$ . With the acetate, in solutions of ordinary strength, excess of ammonium hydroxide (free from carbonate) gives no precipitate, soluble tribasic acetate being formed.

Soluble **carbonates** precipitate *lead basic carbonate, white*, the carbonate and hydroxide combined in proportions varied by conditions. With excess of the reagent, in concentrated solution, the precipitate consists chiefly of  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ . Barium carbonate on boiling precipitates lead salts completely. Free carbonic anhydride precipitates the basic acetate.

**388. Hydrosulphuric acid** and the **sulphides** precipitate—from neutral, acid, or alkaline solutions—*lead sulphide, PbS*, brownish-black, insoluble in highly dilute acids, in alkalis, or alkali sulphides. Freshly precipitated **CdS**, **MnS**, **FeS**, **CoS**, and **NiS**, give the same precipitate.  $\text{H}_2\text{S}$  changes all freshly precipitated lead salts to **PbS**. Moderately dilute (15 to 25 per cent.) nitric acid dissolves lead sulphide, with separation of sulphur (equation *a*); concentrated nitric acid changes it mostly to the (insoluble) lead sulphate (equation *b*)—in both cases with evolution of nitric oxide. The oxidation of the sulphur always occurs in the action of nitric acid on sulphides, in degree proportioned to the strength of acid, temperature, and duration of contact:



In solutions too strongly acidulated, especially with hydrochloric acid, the formation of brick-red basic sulphides, as  $\text{Pb}_2\text{SCl}_2$ , interferes with perfect precipitation; in solutions excessively dilute, only a brown coloration occurs without precipitation. Lead is revealed in solutions in 100,000 parts of water, by this test.

**389. Sulphuric acid** and **sulphates** precipitate, from neutral or acid solutions, *lead sulphate, PbSO<sub>4</sub>*, white, not chemically changed or permanently dissolved by acids, except hydrosulphuric acid, yet slightly soluble in strong acids, as more particularly stated in 386. Soluble in boiling ammonium acetate, and in the fixed alkalis. For solution by transposition into soluble salts, see 396. Soluble in warm sodium thiosulphate solution, at temperatures not above 68° C. (154° F.); (in hot solution, decomposed, **PbS** being one of the products formed, insoluble in thiosulphate); distinction and separation from barium sulphate, which does not dissolve in thiosulphates.



This test is from five to ten times less delicate than that with hydrosulphuric acid; but lead is quantitatively separated as a sulphate, by precipitating with sulphuric acid in presence of alcohol, and washing with alcohol. If the  $\text{PbSO}_4$  is heated with  $\text{K}_2\text{CrO}_4$ , transposition takes place, and the yellow  $\text{PbCrO}_4$  is formed (393). The yellow precipitate is soluble in fixed alkali hydroxides, then reproduced by acetic acid. Also, excess of potassium iodide transposes lead sulphate, the yellow product (392) being a distinction of lead from barium.

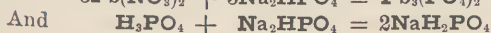
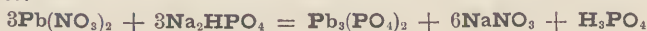
**390. Hydrochloric acid** and soluble **chlorides** precipitate, from solutions not too dilute, *lead chloride*,  $\text{PbCl}_2$ , white. This reaction constitutes lead a member of the **FIRST GROUP**—as it also is of the second. The solubility of the precipitate is such (386) that the filtrate obtained in the cold gives marked reactions with hydrosulphuric acid, sulphuric acid, chromates, etc.; and that it can be quite accurately separated from silver chloride and mercurous chloride by much hot water. Also, small proportions of lead escape detection in the first group, while its *removal is necessarily accomplished in the second group*.

**391. Soluble Bromides** precipitate *lead bromide*,  $\text{PbBr}_2$ , white, soluble in water to about the same extent as the chloride; in concentrated solutions, the precipitate dissolves in excess of the potassium bromide, as  $(\text{KBr})_2\text{PbBr}_2$ , which is decomposed and precipitated by dilution with water. Also soluble in hot solutions of ammonium chloride and nitrate.

**392. Soluble Iodides** precipitate *lead iodide*,  $\text{PbI}_2$ , bright yellow and crystalline, soluble in about 1,900 parts of cold or 200 of hot water; soluble in hot moderately concentrated nitric acid, and in solutions of fixed alkalis not in cold hydrochloric acid; soluble in excess of the alkali iodides, by formation of double iodides—with deficient excess of potassium iodide, forming  $\text{KIPbI}_2$ ; with superabundance of the same reagent, forming  $(\text{KI})_4\text{PbI}_2$ , these double iodides requiring free alkali iodide to hold them in solution, and being partly decomposed by undue addition of water, with reprecipitation of the lead iodide. Lead iodide is not precipitated in presence of sodium citrate; alkaline acetates also hold it in solution to some extent, so that it is less perfectly precipitated from acetate than from nitrate of lead.

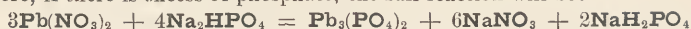
**393. Soluble Chromates**—both  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ —precipitate *lead chromate*,  $\text{PbCrO}_4$ , yellow, soluble in fixed alkali hydrates (distinction from bismuth), insoluble in chromic acid (distinction from barium), slightly soluble in acetic acid, decomposed by hydrochloric acid and by ammonium hydrate.

**394. Disodium hydrogen phosphate** precipitates trimetallic *lead phosphate*,  $\text{Pb}_3(\text{PO}_4)_2$ , white, insoluble in dilute acetic acid (compare 216), soluble in nitric acid and fixed alkalis:





Therefore, if there is excess of phosphate, the full reaction will be:



Alkali **oxalates** precipitate *lead oxalate*,  $\text{PbC}_2\text{O}_4$ , white, insoluble in acetic acid, soluble in potassium and sodium hydroxide solutions, and in nitric acid.

Alkali **sulphites**—as  $\text{Na}_2\text{SO}_3$ —precipitate *lead sulphite*,  $\text{PbSO}_3$ , white, less soluble in water than the sulphate, slightly soluble in sulphurous acid, decomposed by sulphuric, nitric, and hydrochloric acids.

**395. Soluble cyanides**—as **KCN**—precipitate lead cyanide,  $\text{Pb}(\text{CN})_2$ , white, soluble in a very large excess of the reagent, reprecipitated on boiling.—**Ferrocyanides**—as  $\text{K}_4\text{Fe}(\text{CN})_6$ —precipitate *ferrocyanide*,  $\text{Pb}_2\text{Fe}(\text{CN})_6$ , insoluble in dilute acids.—**Ferricyanides** form, in concentrated solutions, a dark brown precipitate, slightly soluble in water.—**Sulphocyanates** form, in concentrated solutions, a yellow crystalline precipitate of *lead sulphocyanate*,  $\text{Pb}(\text{CNS})_2$ , soluble in water, decomposed on boiling, with precipitation of basic sulphocyanate,  $\text{PbOH}(\text{CNS})$ , white.

**396. Tannic acid** precipitates solutions of lead acetate, and partly the nitrate, as yellow-gray tannate of lead, soluble in acids. Solution of lead acetate precipitates a large number—and solution of *lead subacetate* a still larger number—of **organic acids**, color substances, resins, gums, and neutral principles. Indeed, it is a rule, with few exceptions, that lead subacetate removes all organic acids (not acetic, formic, butyric, valeric, or lactic). Ammoniacal solution of lead acetate is used as a reagent, as a form of basic acetate (387).

**397. Lead salts** when fused on porcelain with  $\text{Na}_2\text{CO}_3$  are converted into **PbO** (a). If charcoal is added metallic lead is formed (b). Long continued fusion on charcoal may change the acid radical also (c).



After fusion the aqueous solution is tested for acids and the residue for bases after dissolving in  $\text{HNO}_3$  or  $\text{HC}_2\text{H}_3\text{O}_2$ .

**398. With borax and microcosmic salt**, strictly in the *outer flame*, lead oxide and oxidized compounds give a **bead** yellow when hot, becoming colorless when cold; due to formation of lead borate or phosphate, fused in the glass. If the least reducing action is allowed to bear on the bead, the test is spoiled, and the platinum wire is spoiled likewise. (See under Platinum.)

**399. Estimation.**—(1) As an oxide into which it is converted by ignition (if a carbonate or nitrate), or by precipitation and subsequent ignition. (2) As a sulphate. Add to the solution twice its volume of alcohol, precipitate with  $\text{H}_2\text{SO}_4$ , and after washing with alcohol ignite and weigh. (3) It is converted into an acetate, or sodium acetate is added to the solution, then precipitated with  $\text{K}_2\text{Cr}_2\text{O}_7$ , and after drying at  $100^\circ \text{C}$ . weighed as  $\text{PbCrO}_4$ . (4) It is converted into  $\text{PbS}$ , free sulphur added, and after ignition in hydrogen gas weighed as  $\text{PbS}$ .

**400. Oxidation.**— $\text{Pb}^{\text{II}}$  is oxidized to  $\text{Pb}^{\text{IV}}$ , as stated in (385).  $\text{Pb}^{\text{IV}}$  is reduced to  $\text{Pb}^{\text{II}}$  in presence of dilute  $\text{H}_2\text{SO}_4$  by nascent hydrogen, and by all metals capable of producing nascent hydrogen (such as **Al**, **Zn**, **Sn**, **Mg**, **Fe**), and by soluble compounds of ( $\text{Hg}_2$ )<sup>II</sup>,  $\text{Sn}^{\text{II}}$ ,  $\text{Sb}^{\text{III}}$ ,  $\text{As}^{\text{III}}$ , ( $\text{AsH}_3$  gas),  $\text{Bi}^{\text{III}}$ , ( $\text{Cu}_2$ )<sup>II</sup>,  $\text{Fe}^{\text{II}}$ , ( $\text{Cr}_2$ )<sup>VI</sup>,  $\text{Mn}^{\text{II}}$ ,  $\text{Mn}^{\text{III}}$ ,  $\text{Mn}^{\text{IV}}$ ,  $\text{Mn}^{\text{VI}}$ . Also by  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{HNO}_2$ ,  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_3$ , **P**,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , **HCl**, **HBr**, **HI**, **HCy**, **HCNS**,  $\text{H}_4\text{Fe}(\text{CN})_6$ , glycerine, tartaric acid, sugar, urea, and *very many* organic compounds. In many cases the same reduction takes place in presence of **KOH**.

From lead solutions **Zn**, **Mg**, **Al**, **Co**, and **Cd** precipitate metallic lead. And metallic lead precipitates the free metals from solutions of **Au**, **Pt**, **Ag**, **Hg**, **Bi**, and **Cu**.

**SILVER.**  $\text{Ag} = 107.675$ .

**401. Specific gravity**, precipitated, 10.5532 (G. ROSE, 1848). *Melting point*,  $954^{\circ}\text{C}$ . ( $1749^{\circ}\text{F}$ .) (VIOLE, 1877). Vaporizes at  $1570^{\circ}\text{C}$ . (V. and C. MEYER, 1879). Valence, a monad in  $\text{Ag}'_2\text{O}$  and in silver salts.

**402. Occurrence.**—Found in a free state; oftener in combination; its most important ores are *argentite*, or silver glance ( $\text{Ag}_2\text{S}$ ), *pyrargyrite* ( $\text{Ag}_3\text{SbS}_3$ ), and *horn silver* ( $\text{AgCl}$ ), and it is frequently found in paying quantities in galena ( $\text{PbS}$ ), and copper pyrites, and in many other ores.

**403. Preparation.**—The limits of this work do not permit a description of the metallurgy of silver. Chiefly three methods are employed: (1) It is alloyed with lead by fusion and the lead separated by oxidation. (2) It is amalgamated with mercury and then the mercury separated by distillation. (3) It is brought into solution and the metal precipitated by copper. Silver is very easily *reduced* from its oxide by heat alone, and from *all* its compounds by ignition with  $\text{H}$ ,  $\text{C}$ ,  $\text{CO}$ , and by the organic carbon compound in which the carbon has less than four bonds. It is also reduced without the aid of heat by certain metals, etc. (343).

**404. Properties.**—Silver is the whitest of metals, harder than gold and softer than copper; silver is hardened by copper. United States silver coin contains 90 per cent. silver and 10 per cent. copper. In malleability and ductility it is inferior only to gold; and as a conductor of heat and electricity it exceeds all other metals.

**405. Oxides.**—Silver forms three oxides— $\text{Ag}_2\text{O}$ ,  $\text{Ag}_2\text{O}$ ,  $\text{Ag}_2\text{O}_2$ . *Silver oxide*, argentic oxide ( $\text{Ag}_2\text{O}$ ) is formed by the action of  $\text{KOH}$  or  $\text{NaOH}$  on silver salts or by heating the carbonate to  $200^{\circ}\text{C}$ . It is a brown powder, a strong oxidizing agent, partially decomposed by light, completely decomposed by heat at  $300^{\circ}\text{C}$ . into metallic silver and oxygen. *Argentous oxide* (called also suboxide, quadrantoxide, and tetrantoxide),  $\text{Ag}_4\text{O}$ , is formed by heating silver citrate to  $100^{\circ}\text{C}$ . in hydrogen gas, dissolving in water and precipitating with  $\text{KOH}$ . It is a black powder, easily decomposed by heat, soluble in  $\text{NH}_4\text{OH}$ ; decomposed by oxyacids forming metallic silver and a silver salt; with  $\text{HCl}$  forming argentous chloride ( $\text{Ag}_2\text{Cl}$ ). *Silver peroxide* ( $\text{Ag}_2\text{O}_2$ ) is a black powder formed by treating metallic silver or silver oxide with ozone or peroxide of hydrogen. Oxyacids reduce it, forming a silver salt and evolving oxygen.  $\text{HCl}$  reduces it to  $\text{AgCl}$ , evolving free  $\text{Cl}$ . Silver forms no definite hydroxides.

**406. Solubilities.**—Silver is not **oxidized** by water or air at any temperature, but is oxidized by ozone, is readily attacked by chlorine, bromine, or iodine, and is soon tarnished in air containing hydrosulphuric acid, or in contact with sulphides or certain organic substances containing sulphur, by formation of silver sulphide; also, by substances easily liberating phosphorus, as silver phosphide. As silver is easily reduced from its salts, these act as oxidizing agents of considerable force.

**407.** The proper **solvent** of silver is nitric acid, most efficient when about fifty per cent., but active whether concentrated or dilute—with production of nitric oxide as the chief residual product. Hot concentrated sulphuric acid forms sulphate, which is sparingly soluble; and hot concentrated hydrochloric acid forms silver chloride, slightly soluble in the concentrated reagent, but precipitated on dilution. The fixed alkalies do not act upon silver in the wet or dry way; hence, silver crucibles are used instead of platinum for fusion with caustic alkali. Silver, in the form of a precipitate, is very slowly acted upon by strong aqueous ammonia, dissolving as a nitride.—There is but a single series of **salts** of silver—those represented by  $\text{Ag}'$ , and sometimes designated argentic salts.

**408.** The nitrate, acetate, and sulphate form **permanent** anhydrous crystals. The salts of silver are chiefly **colorless**, except the ortho-phosphate and arsenite, yellow; the

arseniates, reddish-brown; the iodide, yellow; the bromide, yellow-white; the sulphide, black. Normal silver salts do not redden litmus.

**409.** Silver forms a greater number of insoluble salts than any other metal; though, in this respect, there is but little difference between the first-group bases. The oxide, sulphide, chloride, bromide, bromate, iodide, iodate, cyanide, ferrocyanide, ferricyanide, carbonate, oxalate, phosphate, arsenite, arseniate, sulphite, and tartrate are **insoluble** in water; the sulphate is soluble in 200 parts of cold, and less than 100 parts of boiling water. The acetate is soluble in 100 parts of water. The borate, thiosulphate, and citrate are very sparingly soluble in water. The ammonium silver oxide and the numerous ammonium silver salts, the double cyanides, iodides, and thiosulphates of silver and alkaline metals, are soluble in water. The *chloride* is sparingly soluble in strong hydrochloric, nearly insoluble in nitric and dilute sulphuric acids; soluble, to some slight extent, in solutions of all soluble metallic chlorides (except calcium and zinc chlorides), especially soluble with sodium chloride (double chloride being formed); also soluble with certain other alkali salts, and in concentrated solution of mercuric nitrate. The *nitrate* is sparingly soluble in alcohol and in ether, and soluble in glycerine.

**410.** Both the oxy-salts and haloid salts of silver, which are insoluble in water, are *dissolved* by ammonium hydroxide, except the sulphide and iodide; by cold dilute nitric acid, except the chloride, bromide, iodide, bromate, iodate, and the haloids of cyanogen and its compounds; by solution of potassium cyanide, except the sulphide; and by alkali thiosulphates, almost without exception.

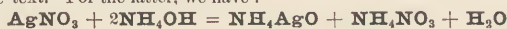
In **analysis**, silver is completely precipitated as a chloride, in the first group (413), and the solubility of this precipitate in ammonium hydroxide separates it from the other first-group bases. Reduction to metallic silver is sometimes employed in analysis (443).

**411.** The **fixed alkali hydroxides** precipitate, from solutions of silver salts (in absence of citrates), *silver oxide*,  $\text{Ag}_2\text{O}$ , grayish-brown (329), insoluble in excess of the reagents; easily soluble in nitric, acetic, and sulphuric acids, and in ammonium hydroxide; somewhat soluble in ammonium salts; soluble in alkali cyanides and thiosulphates; also, soluble in about 3,000 parts of water.

**Ammonium hydroxide**, in neutral solutions of silver nitrate, forms the same precipitate, silver oxide, very easily dissolving in excess, by formation of *ammonium silver oxide*,  $\text{NH}_4\text{AgO}$ .\* In solutions containing much free acid, all precipitation is prevented by the ammonium salt formed.

The ammoniacal solution of silver is not immediately precipitated by addition of excess of fixed alkalies in the cold, but on boiling a black precipitate is formed. From the cold ammoniacal solution containing fixed alkalies a precipitate gradually forms. This precipitate contains *fulminating silver*—a black powder, which explodes with dangerous violence by friction or by drying above ordinary temperatures. Fulminating silver may also be deposited from ammoniacal solutions of silver, on standing, and by digest-

\* This formula accords with the results of a series of volumetric determinations made by Mr. D. E. Osborne and the author (*Jour. Am. Chem. Soc.*, 1880). If silver replaces hydrogen of ammonium, the formula would be  $(\text{NH}_3\text{Ag})_2\text{O}$ —the molecule of which, with a molecule of water, would make two molecules formed as given in the text. For the latter, we have:



ing oxide of silver with strong ammonium hydroxide. Its production, in the way first mentioned, is most favored by a slight excess of the fixed alkali.\*

**412. Hydrosulphuric acid** and alkali sulphides precipitate from neutral, acid, or alkaline solutions, *silver sulphide*,  $\text{Ag}_2\text{S}$ , black, soluble in moderately concentrated nitric acid (distinction from mercury), not in solution of potassium cyanide (distinction from copper); insoluble in alkali sulphides (distinction from tin, etc.)

**413. Hydrochloric acid** and the soluble **chlorides** precipitate *silver chloride*,  $\text{AgCl}$ , white, curdy, separating on shaking the solution; turning violet to brown in the light (from formation of argentous chloride,  $\text{Ag}_2\text{Cl}$ ), very easily soluble in *ammonium hydroxide*, as *ammonio silver chloride*,  $(\text{NH}_3)_3(\text{AgCl})_2$ . The precipitate, also, is slowly soluble in concentrated solution of ammonium carbonate; and is fusible without decomposition. For solubilities of the precipitate—indicating the conditions of delicacy in the test—see 409 and 410. This precipitation is the most delicate of the ordinary tests for silver; being recognized in solution in 250,000 parts of water, and enables us wholly to remove this metal **IN THE FIRST GROUP** of bases.

**414.** Soluble **bromides** precipitate *silver bromide*,  $\text{AgBr}$ , white, with a slight yellowish tint, but slightly soluble in excess of potassium bromide, and much less easily soluble in *ammonium hydroxide* than silver chloride. Soluble **iodides** precipitate *silver iodide*,  $\text{AgI}$ , pale yellow, easily soluble in excess of the reagents by formation of double iodides, as  $\text{KIAgI}$ . The double iodide is decomposed by dilution with much water, and all the silver reprecipitated as iodide. The precipitate is scarcely at all soluble in *ammonium hydroxide* (one part dissolving in 2,600 parts of ten per cent. solution of ammonia). Concentrated nitric acid slowly dissolves it. Regarding other solubilities of argentic bromide and iodide, see 409 and 410.

**415. Potassium cyanide**, or hydrocyanic acid, precipitates, from neutral or slightly acid solutions, *silver cyanide*,  $\text{AgCN}$ , white, quickly soluble in excess of the reagent, as potassium silver cyanide,  $\text{KAg}(\text{CN})_2$ . By formation of these double cyanides, the various compounds of silver are rendered soluble through treatment with alkali cyanides; also, a soluble iodo-cyanide is formed. Silver cyanide is readily soluble in ammonium hydroxide, and promptly decomposed by hydrochloric acid.

**416. Potassium ferrocyanide** precipitates silver ferrocyanide,  $\text{Ag}_4\text{Fe}(\text{CN})_6$ , yellowish-white, diffcultly soluble in ammonium hydroxide; on boiling metallic silver separates and a ferricyanide is formed, not decomposed by hydrochloric acid, changed by nitric acid to the ferricyanide. Exposure

\* The composition of this substance, known as Berthollet's Fulminating Silver, has not been determined, but it contains nitrogen. It is distinct from the silver fulminate,  $\text{Ag}_2\text{CN}_3\text{O}_2$ , represented by fulminic acid, and isomeric with cyanates.



to the air gives it a blue tinge.—**Potassium ferricyanide** precipitates silver ferricyanide, reddish-yellow, soluble in ammonium hydroxide.

**417. Alkali carbonates** precipitate *silver carbonate*,  $\text{Ag}_2\text{CO}_3$ , white or yellowish-white, slightly soluble in water, somewhat soluble in excess of fixed alkali carbonates, quite soluble in ammonium carbonate; soluble in nitric acid and in ammonium hydroxide; changed by boiling to silver oxide. Barium carbonate does not affect solution of silver nitrate.

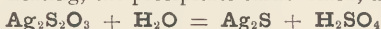
**418. Oxalic acid**, and oxalates, precipitate *silver oxalate*,  $\text{Ag}_2\text{C}_2\text{O}_4$ , white, slightly soluble in water, sparingly soluble by dilute nitric acid, readily soluble in solution of ammonium hydrate. It detonates when heated.

**419. Disodium hydrogen phosphate** precipitates trimetallic *silver ortho-phosphate*,  $\text{Ag}_3\text{PO}_4$ , yellow, soluble in dilute nitric acid, in phosphoric acid, and in ammonium hydrate; but little soluble in dilute acetic acid.—Pyrophosphates—as  $\text{Na}_4\text{P}_2\text{O}_7$ —precipitate silver pyrophosphate,  $\text{Ag}_4\text{P}_2\text{O}_7$ , white, insoluble in acetic acid, soluble in dilute nitric and phosphoric acids, and in ammonium hydroxide.

**420. Arseniates**—as  $\text{Na}_2\text{AsO}_4$ —precipitate red-brown *silver arseniate*,  $\text{Ag}_3\text{AsO}_4$ , having the same solubilities as the ortho-phosphate.—**Arsenites**—as  $\text{Na}_2\text{AsO}_3$ —precipitate silver arsenite,  $\text{Ag}_3\text{AsO}_3$ , yellow, quickly soluble in dilute acids and in ammonium hydroxide.

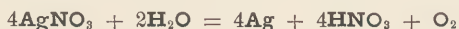
**Chromates**—as  $\text{K}_2\text{CrO}_4$ —precipitate silver chromate,  $\text{Ag}_2\text{CrO}_4$ , dull-red, sparingly soluble in water, not much more soluble in dilute nitric acid.

**Thiosulphates**—as  $\text{Na}_2\text{S}_2\text{O}_3$ —precipitate silver thiosulphate,  $\text{Ag}_2\text{S}_2\text{O}_3$ , white, very instable, and readily soluble in excess of the precipitants, by formation of double thiosulphates. That formed by sodium thiosulphate is first  $\text{NaAgS}_2\text{O}_4$ , with excess of the thiosulphate,  $\text{Na}_4\text{Ag}_2(\text{S}_2\text{O}_3)_3$ ; and corresponding thiosulphates of silver and potassium are formed. By standing or heating, the precipitate turns black, as  $\text{Ag}_2\text{S}$ .



Thiocyanates give **AgCNS**, insoluble in dilute  $\text{HNO}_3$ .

**421.** By a *gradual* reduction of the silver with certain reagents, it is obtained as a bright *silver coating* upon the inner surface of the test-tube, or other glass vessel. A somewhat dilute solution of ammonio nitrate of silver, treated with a dilute alcoholic solution of oils of cloves and cassia—the latter solution not in excess—gives this result. The coating is also obtained by adding to solution of silver nitrate a very little aqueous solution of chloral hydrate, and then a slight excess of ammonia; the ammonium formiate, gradually produced by decomposition of the chloral with alkali, deoxidizes the ammonio silver nitrate. A silver deposit on glass may sometimes be made to assume the form of a compact and lustrous coating, by rubbing with a glass rod. In these deoxidations, generally, the nitric acid radical of silver nitrate is not decomposed, but nitric acid is left.



See, as an example, the statement of the reaction between arsenious hydride and silver nitrate, under Arsenious Acid.

**Light** decomposes most compounds of silver, with blackening from formation of metallic silver or of argentous oxide,  $\text{Ag}_2\text{O}$ , or of both. The nitrate in crystal or pure water solution, the phosphate, iodide, and cyanide, are not decomposed by light alone; but light greatly hastens their decomposition by organic substances, or other reducing agents—as of solution of silver nitrate in rain-water, or written as an ink upon organic fabrics. The base of most indelible inks is silver.

**422.** Silver nitrate and chloride fuse undecomposed, but decompose at a higher heat.



Most silver compounds, heated in the **glass-tube**, leave a metallic residue. On **Charcoal**, with sodium carbonate, silver is reduced from all its compounds in the blow-pipe flame, attested by a bright malleable globule. Lead and zinc, and elements more volatile, may be separated from silver by their gradual vaporization under the blow-pipe. Copper and iron are removed along with larger quantities of lead, previously added for this purpose, either as metallic lead or by reduction from litharge. (See descriptions of *Cupellation*, in works on general chemistry, and more fully in works on assaying of precious metals).

**423.** To identify the acid of silver salts which are insoluble in **HNO<sub>3</sub>** (**AgCl**, **AgBr**, **AgI**), (1) Add metallic zinc and a drop of **H<sub>2</sub>SO<sub>4</sub>**; when the silver is all reduced test for the acid in the filtrate. (2) Fuse with **Na<sub>2</sub>CO<sub>3</sub>**, add water, and test the filtrate for acids. (3) Add **H<sub>2</sub>S**, and proceed in the same manner. (4) Boil with **KOH** or **NaOH** (free from **HCl**), and test the filtrate in the same manner. It must not be overlooked that by the first three methods, and not by the last, bromates and iodates are reduced to bromides and iodides.

**424. Estimation.**—(1) As metallic silver, into which it is converted by direct ignition if it is the oxide or carbonate, or by ignition in hydrogen if the chloride, bromide, iodide, or sulphide. (2) It is precipitated as **AgCl**, and after igniting to incipient fusion (260° C.) weighed. (3) It is converted into **Ag<sub>2</sub>S** by **H<sub>2</sub>S**, and weighed after drying at 100° C. Inadmissible in case of an acid that might liberate free sulphur. (4) Add **KCN** until a solution of **KAg(CN)<sub>2</sub>** is formed, precipitate with **HNO<sub>3</sub>**, and after drying at 100° C. weigh as **AgCN**. (5) Volumetrically, by adding a graduated solution of **NaCl** until a precipitate is no longer formed. This may be varied by adding the measured silver solution to the graduated **NaCl** solution, containing a few drops of **K<sub>2</sub>CrO<sub>4</sub>**, until the red precipitate begins to form. (6) Volumetrically, add a graduated solution of ammonium thiocyanate, containing ferric sulphate, until the red color ceases to disappear.

**425. Oxidation.**—Metallic silver precipitates gold and platinum from their solutions, and is precipitated as metallic silver from its solutions by **Zn**, **Mg**, **Al**, **Cd**, **Pb**, **Cu**, (**Cu<sub>2</sub>**)', **Sn**, **Sn'**, **Hg**, **Bi**, **Te**, **Sb**, **SbH<sub>3</sub>**, **As**, **AsH<sub>3</sub>**, **P**, **H<sub>3</sub>PO<sub>2</sub>**, **H<sub>2</sub>SO<sub>3</sub>**, and is reduced in presence of **KOH** by (**Hg<sub>2</sub>**)', **Sn'**, **As'''**, **Sb'''**, **Bi'**, **Mn'**, and (**Cu<sub>2</sub>**)'. Also by **FeSO<sub>4</sub>** when cold (incompletely), and redissolved on boiling, the ferric sulphate first formed being again reduced to **FeSO<sub>4</sub>**.

## MERCURY. Hg = 199.712.

**426. Specific gravity**, liquid, 13.596 (VOLKMANN, 1881); solid, 14.193 (MALLET, 1877). *Melting (freezing) point*, -38.8° C. (-38° F.) STEWART. *Boiling point*, 357.25° C. (675° F.) (REGNAULT, 1860). *Vapor density* (**H** = 1), 200.93 (V. MEYER, 1880). Valence, a dyad in **Hg''O** and in *mercuric* salts; a pseudo-monad in (**Hg<sub>2</sub>**)''**O**, and in *mercurous* salts.

**427. Occurrence.**—Found native, but its chief ore is cinnabar (**HgS**). It is also found as **Hg<sub>2</sub>Cl<sub>2</sub>** and as an amalgam with gold and silver.

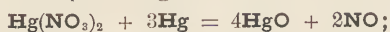
**Preparation.**—From **HgS**. (1) It is roasted in the air; **HgS** + **O<sub>2</sub>** = **Hg** + **SO<sub>2</sub>**. (2) Lime is added and the mercury distilled; **4HgS** + **4CaO** = **3CaS** + **CaSO<sub>4</sub>** + **4Hg**.

**428. Properties.**—It is the only metal which is a liquid at ordinary temperatures; white when pure, and having a brilliant silvery lustre. It is slightly volatile at ordinary temperatures. Divided in globules invisible to the unaided eye, and separated by minute films of liquid or solid foreign

matter, mercury appears as a dark gray powder. It is not **oxidized** by agitation with air or oxygen—the tarnish acquired on the surface of commercial mercury, by exposure to the atmosphere, being due to intermixture of foreign metals; but by agitation with water, or with various substances, the metal is “extinguished,” or divided to the gray pulverulent form, which contains some mercurous oxide when so prepared. Also, the gray pulverulent mercury is precipitated by reduction from salts in solution. Aqueous solutions of alkali chlorides, with access of the air, gradually act upon mercury by formation of mercuric chloride. Solution of potassium permanganate oxidizes mercury—forming mercurous oxide, manganic hydroxide and potassium hydroxide.

**429. Solubilities.**—The most effective solvent of mercury is **nitric acid**. It dissolves readily in the dilute acid hot or cold; with the strong acid, heat is soon generated; and with considerable quantities of material, the action acquires an explosive violence. At ordinary temperatures, nitric acid, when applied in excess, produces normal mercuric nitrate, but when the mercury is in excess, mercurous nitrate is formed; in all cases, chiefly nitric oxide gas is generated. Both mercurous and mercuric nitrates require a little free nitric acid to hold them in solution. This free nitric acid gradually oxidizes mercurous to mercuric, making a clear solution of  $\text{Hg}(\text{NO}_3)_2$ , if there is sufficient  $\text{HNO}_3$  present, otherwise a basic mercuric nitrate may precipitate. A solution of mercurous nitrate may be kept free from mercuric nitrate by placing some *metallic* mercury in the bottle containing it; still after standing some weeks a basic mercurous nitrate crystallizes out, which a fresh supply of nitric acid will dissolve. **Chlorine**—in aqueous solution, or formed in nitro-hydrochloric acid—dissolves mercury slowly, to mercuric chloride. **Hydrochloric acid** does not dissolve mercury. **Bromine** and **iodine** promptly unite with mercury. Dilute **sulphuric acid** does not act upon mercury; but the concentrated acid, when heated, dissolves it with moderate rapidity, evolving sulphurous anhydride.

**430. Oxides.**—*Mercurous oxide* ( $\text{Hg}_2\text{O}$ ) is formed by treating mercurous oxy-salts or  $\text{Hg}_2\text{Cl}_2$  with **KOH** or **NaOH**. It is a black powder which a gentle heat changes to  $\text{HgO}$  and  $\text{Hg}$ , and a higher heat into  $\text{Hg}$  and  $\text{O}$ . *Mercuric oxide*,  $\text{HgO}$ , is made (1) by keeping  $\text{Hg}^\circ$  at its boiling point for a month or longer in a flask filled with air; (2) by heating  $\text{Hg}_2(\text{NO}_3)_2$  or  $\text{Hg}(\text{NO}_3)_2$  with about an equal weight of metallic mercury,



(3) by precipitating mercuric salts with **KOH** or **NaOH**. Made by (1) and (2) it is red, by (3) yellow. On heating it changes to vermilion red, then black, and on cooling regains its original color. A red heat decomposes it completely into  $\text{Hg}^\circ$  and  $\text{O}^\circ$ . Mercury forms no hydroxides.

**431.** Mercury forms two well-marked **classes of salts**—mercurous and mercuric;—mercurous compounds being permanent in the air, but changed

by powerful oxidizing agents to mercuric compounds. The latter are somewhat more stable, but act as oxidizing agents in many relations. Mercury as a noble metal is not strongly electro-positive; and many reducing agents change mercuric compounds, first to mercurous combinations, and then to metallic mercury.

Solutions of mercurous and mercuric salts redden **litmus**. Mercuric chloride is **permanent**; nitrate, deliquescent.

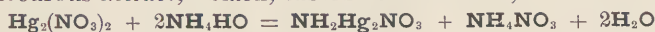
**432. MERCUROUS** compounds, of ordinary occurrence, are **insoluble** in water, except the normal nitrate; the sulphate and the acetate are sparingly soluble (that is, in 300 to 600 parts of water). And these require acidulated water for their full solution; becoming *decomposed by water*, at a certain degree of dilution, with precipitation of basic salts (326).

*Mercurous chloride* is very slowly soluble by cold concentrated solutions of alkali chlorides, somewhat more rapidly when heated, the solution being due to formation of mercuric chloride and mercury. Dilute hydrochloric acid, at ordinary temperatures, fails to dissolve mercurous chloride; but when heated it gradually causes the formation of mercuric chloride and mercury, the action being very slow with dilute acid, tolerably rapid with concentrated acid. In presence of certain organic substances, the resolution into mercuric chloride and mercury takes place at 38° to 40° C. (100° F.) Free **chlorine**, and **nitric acid**, quickly dissolve mercurous chloride, as mercuric salt.

In **analysis**, mercurous compounds are precipitated, from solution, as chloride, in the first group, and this precipitate is distinguished from others in the group, by blackening with ammonium hydroxide. The identification of mercury, by reduction to metallic state, is the same as with mercuric compounds.

**433. Reactions of mercurous salts.**—Fixed alkali hydroxides precipitate from solutions of mercurous salts, *mercurous oxide*,  $\text{Hg}_2\text{O}$ , black, insoluble in alkalies.

Solution of **ammonium hydroxide** produces black precipitates; that from solution of mercurous nitrate being  $(\text{NH}_2\text{Hg}_2)\text{NO}_3$ , nitrogen dihydrogen dimercurous nitrate,\* black, insoluble in alkalies, soluble in acids:



Mercurous chloride, white, is changed by ammonium hydroxide to  $(\text{NH}_2\text{Hg}_2)\text{Cl}$ , nitrogen dihydrogen dimercurous chloride, or dimercurous

\* The compounds produced by action of ammonium hydroxide on mercury compounds are considered as substitutions of  $\text{Hg}$  for a certain number of atoms of  $\text{H}$  in  $\text{NH}_4$  (ammonium). The substitutions formed from *mercurous* compounds contain (200 parts by weight or) one atom of  $\text{Hg}$  (acting as a monad) for each atom (1 part) of  $\text{H}$  displaced; they are termed mercurous-ammoniums; mercurousammonium being  $\text{NH}_2\text{Hg}$ ; di-mercurousammonium,  $\text{NH}_2\text{Hg}_2$ ; tri-mercurousammonium,  $\text{NH}\text{Hg}_3$ , etc. The substitutions formed in ammonium by mercury from *mercuric* compounds contain one atom of  $\text{Hg}$  (acting as a dyad) for two atoms of  $\text{H}$  displaced; they are designated as mercurammoniums; mercurammonium being  $(\text{NH}_2)_2\text{Hg}$ ; di-mercurammonium,  $\text{NH}_2\text{Hg}_2$ ; tri-mercurammonium,  $(\text{NH})_2\text{Hg}_3$ ; tetra-mercurammonium,  $\text{NH}\text{Hg}_4$ .

ammonium chloride, black (distinction from lead), decomposed by acids, insoluble in ammonium hydroxide (distinction from silver) :



434. Solutions of the carbonates of the fixed alkali metals precipitate an instable mercurous carbonate,  $\text{Hg}_2\text{CO}_3$ , gray, blackening to basic carbonate and oxide when heated. Ammonium carbonate reacts like ammonium hydroxide.  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{MgCO}_3$  precipitate mercurous salts, in the cold.

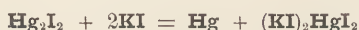
435. Hydrosulphuric acid, and soluble sulphides, precipitate, not  $\text{Hg}_2\text{S}$ , but  $\text{HgS} + \text{Hg}$ , insoluble in  $(\text{NH}_4)_2\text{S}$ , but normal  $\text{K}_2\text{S}$ , in presence of  $\text{KOH}$ , dissolves the  $\text{HgS}$ , and leaves the  $\text{Hg}$  as a residue.

436. Hydrochloric acid and soluble chlorides form a white precipitate of mercurous chloride,  $\text{Hg}_2\text{Cl}_2$ , "calomel"—placing the mercurous base **IN THE FIRST GROUP**. For relations of the precipitate to solvents, see 432 ; to ammonium hydrate, see 433 ; fixed alkalies blacken it by formation of  $\text{Hg}_2\text{O}$  (433).

437. Soluble bromides precipitate mercurous bromide,  $\text{Hg}_2\text{Br}_2$ , yellowish white, insoluble in water and in alcohol, insoluble in dilute nitric acid.

438. Soluble iodides precipitate mercurous iodide,  $\text{Hg}_2\text{I}_2$ , greenish-yellow—"the green iodide of mercury." The precipitate from mercurous nitrate contains more or less mercuric iodide ; that from the acetate is nearly pure  $\text{Hg}_2\text{I}_2$ .

Mercurous iodide is nearly insoluble in water, insoluble in alcohol (distinction from mercuric iodide), somewhat soluble in ether, slowly soluble in part by aqueous solutions of alkali iodides (excess of the precipitants), being first decomposed to mercuric iodide and mercury, which last remains undissolved :



Ammonium hydroxide solution slowly decomposes and partially dissolves mercurous iodide.

By sublimation, and to some extent by exposure to light, mercurous iodide is changed to mercurous-mercuric iodide,  $\text{HgI.HgI}_2$ , yellow—with separation of metallic mercury. When the precipitate by iodide of potassium, in solution of mercurous nitrate, is made in very dilute solutions or is allowed to stand for some time, it consists chiefly of this—"the yellow iodide of mercury." It is strictly insoluble in alcohol; melts and sublimes undecomposed, and is affected by alkali iodides like mercurous iodide.

439. Alkali cyanides, also hydrocyanic acid, resolve mercurous salts into metallic mercury, a gray precipitate, and mercuric cyanide, which remains in solution.—**Ferrocyanides** form a white, gelatinous; **ferricyanides**, a red-brown precipitate.

Alkali phosphates—as  $\text{Na}_2\text{HPO}_4$ —precipitate the white mercurous phosphate,  $\text{Hg}_3\text{PO}_4$ , when the reagent is added in excess; the yellow mercurous phosphate-nitrate,  $\text{Hg}_3\text{PO}_4.\text{HgNO}_3$ , when mercurous nitrate is in excess.—**Chromates** precipitate the orange-yellow mercurous chromate, basic; changed by dilute nitric acid to the normal  $\text{Hg}_2\text{CrO}_4$ ; by strong nitric acid changed to mercuric chromate, and dissolved.—Oxalic acid and oxalates precipitate the white mercurous oxalate,  $\text{Hg}_2\text{C}_2\text{O}_4$ , slightly soluble in dilute nitric acid.



Soluble **sulphates** precipitate, from solutions not dilute, the white *mercurous sulphate*,  $\text{Hg}_2\text{SO}_4$ , sparingly soluble in water (432); decomposed by boiling water with precipitation of a basic sulphate; more soluble in dilute nitric acid; blackened by ammonium hydroxide and fixed alkalies (distinction from other sparingly soluble sulphates).

**440.** Mercurous compounds are **reduced** to metal by the same reducing agents that reduce mercuric compounds to metal; but not by all the reducing agents capable of converting mercuric to mercurous combinations, as more fully specified in 448. As to oxidation of mercurous compounds, see 451.—The reactions in the **dry way** are nearly the same as those for mercuric compounds (449).

**441. MERCURIC** oxide, sulphide, iodide, iodate, basic carbonate, oxalate, phosphate, arseniate, arsenite, ferrocyanide, and tartrate are **insoluble** in water. The bromide is soluble in 250 parts of cold, or one-tenth that proportion of boiling water. The acetate and cyanide are freely, the chromate and citrate sparingly, soluble in water. The double iodides of mercury, and the metals of the alkalies and alkaline earths, are soluble in water—that is, mercuric iodide is soluble in aqueous solutions of alkali iodides. The double bromides dissolve in a smaller proportion of water than the bromide. Except the chloride, the ordinary mercuric salts which are soluble in water are so only by presence of free acid being partially *decomposed by water*, with separation of basic salts (326). In work with solution of mercuric nitrate, some of the reactions are modified by the free acid, always present.—Mercuric sulphate is soluble in very dilute sulphuric acid.—The *chloride* is soluble in about 12 parts of cold, or two to three parts of boiling water; freely soluble in alcohol and in ether.

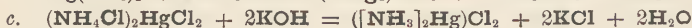
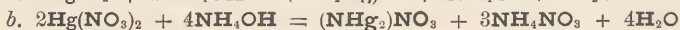
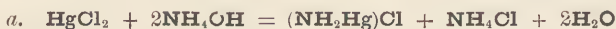
In **analysis**, the second-group precipitate of mercury sulphide is separated by its insolubility in dilute nitric acid. The final form, in determination of mercury, is usually the metallic state (448 *a*, or 449).

**442. Reactions of mercuric salts.**—Solutions of the **fixed alkali hydroxides**, added, short of saturation, to solutions of mercuric salts, precipitate reddish-brown *basic salts*; when the reagent is added to supersaturation, the orange-yellow *mercuric oxide*,  $\text{HgO}$ , is precipitated. Prepared in the dry way, mercuric oxide is obtained red—the “red precipitate” of the shops. From very acid solutions, the precipitate is incomplete or does not form at all, owing to its solubility in alkali salts. It is very slightly soluble in water. In presence of an ammonium salt, the white precipitate (443) is formed. Certain organic acids interfere with the precipitation.

**443. Ammonium hydroxide** produces a “white precipitate,” recognizable in very dilute solutions; that with neutral solution of mercuric chloride being  $(\text{NH}_2\text{Hg})\text{Cl}$ , nitrogen dihydrogen mercuric chloride (*a*); that with hot dilute solution of mercuric nitrate and excess of ammonia being  $(\text{NHg}_2)\text{NO}_3$ , nitrogen dimercuric nitrate (*b*). The precipitates are easily soluble in hydrochloric acid; sparingly soluble in strong ammonium



hydroxide, which should not be used in excess in precipitation. They are also more or less soluble in ammonium salts, and especially in ammonium nitrate. Therefore, the precipitation by ammonium hydroxide is always in some degree incomplete; and that of the acid mercuric nitrate is decidedly diminished, and in very dilute solutions prevented altogether, by the ammonium salt formed in the reaction (as shown in equations *a* and *b*). A soluble combination of ammonium chloride with mercuric chloride,  $(\text{NH}_4\text{Cl})_2\text{HgCl}_2$ , or ammonium mercuric chloride, called “sal alembroth,” is not precipitated by ammonium hydroxide, but potassium hydroxide precipitates therefrom the white mercurammonium chloride,  $(\text{N}_2\text{H}_6\text{Hg})\text{Cl}_2$  (*c*).

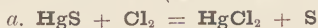


Ammonium carbonate reacts like ammonium hydrate.

444. Potassium and sodium carbonates precipitate first red-brown *basic salts*, which, by excess of the precipitants with heat, are converted into the yellow mercuric oxide. The basic salt formed with mercuric chloride is an oxychloride,  $\text{HgCl}_2 \cdot (\text{HgO})_{2, 3, \text{ or } 4}$ ; with mercuric nitrate, a basic carbonate,  $(\text{HgO})_3\text{HgCO}_3$  or  $(\text{HgO})_4\text{CO}_2$  — Barium carbonate precipitates a basic salt in the cold, from the nitrate, but not from the chloride.

445. Hydrosulphuric acid, gradually added to solutions of mercuric salts, forms at first a white precipitate, soluble in acids and in excess of the mercuric salt; by further additions of the reagent, the precipitate becomes yellow-orange, then brown, and finally black, insoluble in hydrochloric or dilute nitric acid. This progressive variation of color is characteristic of mercury, and is also produced by ammonium sulphide. The final and stable precipitate is *mercuric sulphide*,  $\text{HgS}$ ; the lighter colored precipitates consist of unions of the original mercuric salt with mercuric sulphide, as  $\text{HgCl}_2 \cdot \text{HgS}$ , the proportion of  $\text{HgS}$  being greater with the darker precipitates. When sublimed and triturated, the black mercuric sulphide is converted to the red (vermilion), without chemical change.

*Mercuric sulphide* is soluble by free chlorine (nitro-hydrochloric acid) (*a*); not affected by dilute nitric acid (distinction from all other metallic sulphides) or by hydrochloric acid; insoluble in ammonium sulphide (distinction from tin, antimony, arsenic); insoluble in  $\text{NaOH}$ , and in  $\text{Na}_2\text{S}$ , but dissolves in a mixture of the two (M. C. MEHU, J. B., 1876).



446. Soluble bromides precipitate, from concentrated solutions of mercuric salts, the white  $\text{HgBr}_2$ , soluble in 25 parts of hot and in 250 parts of cold water. Also soluble in excess of mercuric salts, and in excess of the bromide by which the precipitate is formed; hence, unless added in suitable proportions, no precipitate will be produced. The precipitate is decomposed by strong or hot nitric acid.

Soluble **iodides** precipitate *mercuric iodide*,  $\text{HgI}_2$ , first reddish-yellow, then red; very slightly soluble in water, soluble in concentrated nitric and hydrochloric acids; quickly soluble in solutions of the iodides of all the more positive metals—that is, in excess of its precipitants, by formation of soluble *double iodides*; as  $(\text{KI})_2\text{HgI}_2$  variable to  $\text{KI}.\text{HgI}_2$ .\*

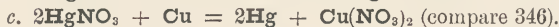
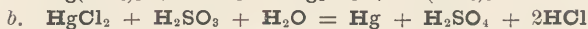
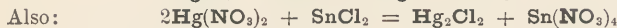
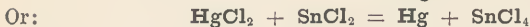
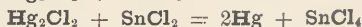
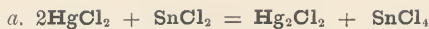
The dipotassium mercuric tetraiodide ( $\text{K}_2\text{HgI}_4$ ) (sometimes designated the iodo-hydrargyrate of potassium) is precipitated by **ammonium hydroxide**, and by the alkaloids (see Nessler's Test, 40). Dilute acids precipitate the mercuric iodide.

**447.** Soluble normal **chromates** precipitate, from very concentrated solutions, basic mercuric chromates, orange yellow to red; considerably soluble in water, more soluble in solution of mercuric chloride or nitrate. Soluble **phosphates**, as  $\text{Na}_2\text{HPO}_4$ , precipitate **mercuric phosphate**,  $\text{Hg}_3(\text{PO}_4)_2$ , white, soluble in acids, including phosphoric acid, and in ammonium salts. Soluble **oxalates**, and oxalic acid, precipitate—from the nitrate, but not from the chloride—*mercuric oxalate*,  $\text{HgC}_2\text{O}_4$ , white, readily soluble in dilute hydrochloric acid, difficultly soluble in nitric acid.  $\text{HgCl}_2$  boiled in the sunlight with  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  gives  $\text{Hg}_2\text{Cl}_2$  and  $\text{CO}_2$ . **Potassium Ferrocyanide** precipitates mercuric ferrocyanide, white, becoming blue on standing.

**448.** **Reducing agents** precipitate, from the solutions of mercuric and mercurous nitrates, *dark-gray*  $\text{Hg}^\circ$ ; from solution of mercuric chloride, or in presence of chlorides, *first the white*,  $\text{Hg}_2\text{Cl}_2$ , *then gray*  $\text{Hg}$ . Strong acidulation with nitric acid interferes with the reduction, and heating promotes it. By digestion with hot concentrated hydrochloric acid—and a little solution of stannous chloride—the gray precipitate of divided mercury is converted into liquid globules of metallic lustre. This somewhat tardy result is hastened by trituration with a glass rod in the test-tube; or first wash and then dry, when trituration will accomplish the object at once.

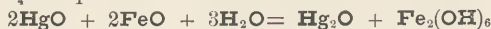
The reducing agent most frequently employed is **stannous chloride** (*a*). Boiling solution of sulphurous acid (*b*) effects the reduction. A clean strip of **copper**, placed in a slightly acid solution of a salt of mercury, becomes coated with metallic mercury, and when gently rubbed with cloth or paper presents the tin-white lustre of the metal (*c*), the coating being driven off by heat. Zinc and iron, also, reduce mercury, and from mercuric chloride or in presence of chlorides, first precipitate calomel. Formic acid reduces mercuric to mercurous chloride, and in the cold does not effect further reduction. Dry mercuric chloride, moistened with alcohol, is reduced by metallic *iron*, a bright strip of which is corroded soon after immersion into the powder tested (a delicate distinction from mercurous chloride).

\* A hot concentrated solution of potassium iodide dissolves  $3\text{HgI}_2$  for every  $2\text{KI}$ . The first crystals from this solution are  $\text{KI}.\text{HgI}_2$ . These are decomposed by pure water, and require a little free iodide for perfect water solution, but they are soluble in alcohol and in ether.

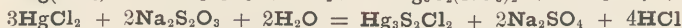
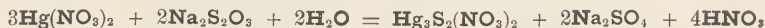


**449.** All compounds of mercury, in glass tubes or on charcoal, are quickly *volatile* before the **blow-pipe**. Mercurous chloride and bromide and mercuric chloride and iodide sublime (in glass tubes) *undecomposed*—the sublimate condensing (in the cold part of the tube) without change. Most other compounds of mercury are decomposed by vaporization, and give a sublimate of metallic mercury (mixed with sulphur, if from the sulphide, etc.) All compounds of mercury, dry and intimately mixed with dry **sodium carbonate**, and heated in a glass tube closed at one end, give a sublimate of metallic mercury as a gray mirror coat on the inner surface of the cold part of the tube. Under the magnifier, the coating is seen to consist of globules, and by gently rubbing with a glass rod or a wire, globules visible to the unaided eye are obtained.

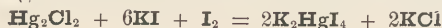
**450. Estimation.**—(1) As metallic mercury. The mercury is reduced by means of **CaO** in a combustion-tube at a red heat in a current of **CO**<sub>2</sub>. The sublimed mercury is condensed in a flask of water, and, after decanting the water, dried in a bell-jar over sulphuric acid without application of heat. The mercury may also be reduced from its solution by **SnCl**<sub>2</sub> (or **H**<sub>3**PO**<sub>3</sub> at 100° C.) and dried as above. (2) As mercurous chloride. It is first reduced to (**Hg**<sub>2</sub>)'' by **H**<sub>3**PO**<sub>3</sub>, which must not be heated above 60° C., otherwise metallic mercury will be formed; and after precipitation by **HCl** and drying on a weighed filter at 100° C. it is weighed as **Hg**<sub>2</sub>**Cl**<sub>2</sub>. Or enough **HCl** is added to combine with the mercury, then the **Hg**'' is reduced to (**Hg**<sub>2</sub>)'' by **FeSO**<sub>4</sub> in presence of **NaOH**.</sub></sub>



**H**<sub>2</sub>**SO**<sub>4</sub> is added, which causes the formation of **Hg**<sub>2</sub>**Cl**<sub>2</sub>, which is dried on a weighed filter at 100° C. (3) As **HgS**. It is precipitated by **H**<sub>2</sub>**S**, and weighed in same manner as the chloride. Any free sulphur mixed with the precipitate should be removed by **CS**<sub>2</sub> or **Na**<sub>2</sub>**S**<sub>2</sub>**O**<sub>3</sub>. (4) As **HgO**, by heating the nitrate in a bulb-tube in a current of dry air not hot enough to decompose the **HgO**. (5) Volumetrically, by **Na**<sub>2</sub>**S**<sub>2</sub>**O**<sub>3</sub>; from the *nitrate* the precipitate is *yellow*, from the *chloride* it is *white*.



(6) Volumetrically, **HgCl**<sub>2</sub> is reduced to **Hg**<sub>2</sub>**O** by **FeSO**<sub>4</sub> in presence of **KOH**, and after acidulating with **H**<sub>2</sub>**SO**<sub>4</sub> the excess of **FeSO**<sub>4</sub> is determined by **K**<sub>2</sub>**Cr**<sub>2</sub>**O**<sub>7</sub> or **K**<sub>2</sub>**Mn**<sub>2</sub>**O**<sub>8</sub>. (7) By iodine. It is converted into **Hg**<sub>2</sub>**Cl**<sub>2</sub> and then dissolved in a graduated solution of **I** dissolved in **KI**.



The excess of iodine is determined by  $\text{Na}_2\text{S}_2\text{O}_3$ . (8) The measured solution of  $\text{HgCl}_2$  is added to a graduated solution of  $\text{KI}$ ;  $4\text{KI} + \text{HgCl}_2 = \text{K}_2\text{HgI}_4 + 2\text{KCl}$ . The instant the amount of  $\text{HgCl}_2$  shown in the equation is exceeded a red precipitate of  $\text{HgI}_2$  appears.

**451. Oxidation.**—Free mercury ( $\text{Hg}^\circ$ ) precipitates the free metals from solutions of **Ag**, **Au**, and **Pt**; and is precipitated as  $\text{Hg}^\circ$  by **Zn**, **Al**, **Mg**, **Cd**, **Bi**, **Co**, **Sn**, **Sn''**, **Cu**, and  $(\text{Cu}_2)''$ , also by free  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_3$ , and  $\text{H}_2\text{SO}_3$ .  $(\text{Hg}_2)''$  is oxidized to  $\text{Hg}''$  by **Br**, **Cl**, **I**,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  (hot), and  $\text{HClO}_3$ .

452. Comparison of Certain Reactions of First-Group Metals.  
*Taken in Solution of their Nitrates or Acetates.*

	Pb	Ag	(Hg <sub>2</sub> )''	Hg''
KOH or NaOH in excess.....	Solution (387).	Ag <sub>2</sub> O, grayish brown (411).	Hg <sub>2</sub> O, black (433).	HgO, yellow to red (442).
NH <sub>4</sub> OH in excess.....	White precipitate. Not formed in the acetate (387).	Solution (411).	(NH <sub>4</sub> Hg <sub>2</sub> )NO <sub>3</sub> , black (435).	(NH <sub>4</sub> Hg <sub>2</sub> )NO <sub>3</sub> , white; (NH <sub>2</sub> Hg)Cl, white (443).
Chlorides.....	PbCl <sub>2</sub> , sparingly soluble in water, more freely if hot (390).	AgCl, white (413).	Hg <sub>2</sub> Cl <sub>2</sub> , white, dissolved by oxidizing acids (436).	Solution.
Bromides.....	PbBr <sub>2</sub> , slightly soluble in water (391).	AgBr, pale yellowish-white (414).	Hg <sub>2</sub> Br <sub>2</sub> , yellowish-white (437).	(446).
Iodides.....	PbI <sub>2</sub> , orange-yellow, sparingly soluble in alkali iodides (392).	AgI, pale-yellow, freely soluble in alkali iodides (414).	Hg <sub>2</sub> I <sub>2</sub> , yellowish-green, decomposed by alkali iodides (438).	Hg <sub>2</sub> I <sub>2</sub> , red, freely soluble in alkali iodides (446).
H <sub>2</sub> SO <sub>4</sub> and Sulphates.....	PbSO <sub>4</sub> , least soluble sulphate except barium (389).	No precip., except in concentrated solutions (328).	No precipitate in dilute solutions (439).	Solution requires a little free acid (441).
Chromates.....	PbCrO <sub>4</sub> , yellow (393).	Ag <sub>2</sub> CrO <sub>4</sub> , purple-red (420).	Hg <sub>2</sub> CrO <sub>4</sub> , orange-yellow (439).	Precipitate only in concentrated solutions (447).
Zinc.....	Pb (400).	Ag (425).	Hg (448).	Hg'' <sub>2</sub> salts, then Hg (448).
Lead.....	.....	Ag.	Hg.	Hg'' <sub>2</sub> salts, then Hg (448).
Mercury.....	.....	Ag.	.....	.....
Stannous Salts.....	.....	Ag.	Hg.	(Hg <sub>2</sub> )'' salts, then Hg.



ARSENIC.  $\text{As} = 74.918$ .

**453. Specific gravity**, pure crystalline, 4.71 (BETTENDORF, 1867); after fusion, under great pressure, 5.71 (MALLET, 1872). *Vapor density* ( $\text{H} = 1$ ) 147.2 (DEVILLE and TROOST, 1863); therefore the molecule is assumed to contain four atoms ( $\text{As}_4$ ). Volatilizes in an atmosphere of coal-gas without melting at  $450^\circ \text{C}$ . (CONECHY, 1880). Fuses under great pressure between the melting point of **Ag** and **Sb** (MALLET, 1872). Valence, a pentad in  $\text{H}_3\text{As}^{\text{V}}\text{O}_4$ ; a triad in  $\text{As}_4\text{O}_6$ ; oxidation valence in free arsenic, zero ( $\text{As}^0$ ), and in arsenious hydride a negative triad ( $\text{As}^{-'''}\text{H}_3$ ).

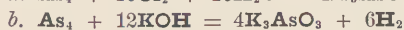
**454. Occurrence.**—Found native; also as an alloy with other metals, as  $\text{FeAs}_2$ ,  $\text{NiAs}$ ,  $\text{CoNiAs}_2$ ; as realgar ( $\text{As}_2\text{S}_2$ ), orpiment ( $\text{As}_2\text{S}_3$ ), and mispickel ( $\text{Fe}_2\text{AsS}_2$ ). It is sometimes found as  $\text{As}_4\text{O}_6$ , as an arsenate in cobalt bloom ( $\text{Co}_3(\text{AsO}_4)_2$ ), and in a great variety of minerals.

**Preparation.**—(1) Reduced from its oxide by carbon,  $\text{As}_4\text{O}_6 + 3\text{C} = \text{As}_4 + 3\text{CO}_2$ . (2) From  $\text{Fe}_2\text{AsS}_2$  by simple ignition, air being excluded,  $4\text{Fe}_2\text{AsS}_2 = 8\text{FeS} + \text{As}_4$ . (3) From  $\text{As}_2\text{S}_3$  by fusion with  $\text{Na}_2\text{CO}_3$  and **KCN**.



**455. Properties.**—Arsenic is by some chemists classed with metals, by others with the non-metallic elements. Its failure to act as a base with oxyacids determines definitely its non-metallic character.

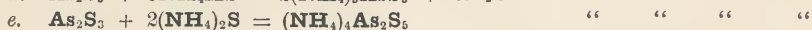
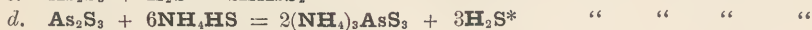
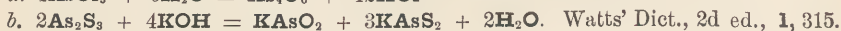
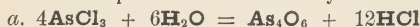
The amorphous arsenic is black, the crystalline a steel-gray, brittle and pulverizable. Its vapor is yellow, with a strong oppressive and poisonous alliaceous odor. It is slowly **oxidized** in moist (not in dry) air at ordinary temperatures; when heated in the air, it burns with a bluish flame, and becomes the white arsenious anhydride,  $\text{As}_4\text{O}_6$ . It readily combines with chlorine and bromine upon contact, and with iodine and sulphur by aid of heat. It is not attacked by aqueous hydrochloric acid at ordinary temperatures, and but slightly when hot and concentrated and with air; it is slowly oxidized to arsenic acid by hot concentrated sulphuric acid, or more readily by nitric acid; but its proper **solvent** is nitro-hydrochloric acid, or chlorine with water, by which it is oxidized to arsenic acid with violent rapidity (*a*). Hot solution of potassium or sodium hydrate dissolves it as arsenite (*b*):



Arsenic forms two **oxides**, both acidulous: *arsenious anhydride*,  $\text{As}^{\text{III}}_4\text{O}_6$ , representing a series of arsenious compounds and arsenites of metals; and *arsenic anhydride*,  $\text{As}^{\text{V}}_4\text{O}_{10}$ , forming arsenates of metals, and arsenic acids, and representing other arsenic compounds. Both these classes of compounds possess considerable stability; the arsenious bodies acting as efficient reducing agents, and the arsenic substances, with less activity, as oxidizing agents.

**456. ARSENIOS ACID AND ANHYDRIDE.**—The vapor density of the anhydride (arsenious oxide) is 198 at a white heat (V. MEYER, *Ber. Chem. Ges.*, 1879, 1117), therefore its molecule is assumed to be  $\text{As}_4\text{O}_6$ . Its solution in water is supposed to be arsenious acid, but on evaporation only  $\text{As}_4\text{O}_6$  remains. Many arsenites are known, but the instability of the greater number of them has prevented an accurate determination of their composition. Their composition is best explained by regarding them as derived from one of the three hypothetical arsenious acids. (1) *Orthoarsenious acid*,  $\text{H}_3\text{AsO}_3$ ; forming normal, acid, and basic *orthoarsenites*—e.g.,  $\text{Ag}_3\text{AsO}_3$ ,  $\text{Mg}_3(\text{AsO}_3)_2$ ,  $\text{Co}_3\text{H}_6(\text{AsO}_3)_4$ ,  $\text{CuHAsO}_3$ ,  $\text{Fe}_8\text{O}_9(\text{AsO}_3)_2$ , etc. (2) *Pyroarsenious acid*,  $\text{H}_4\text{As}_2\text{O}_5$ ; forming *pyroarsenites*—e.g.,  $(\text{NH}_4)_4\text{As}_2\text{O}_5$ ,  $\text{Ca}_2\text{As}_2\text{O}_5$ ,  $\text{K}_4\text{As}_2\text{O}_5$ , etc. (3) *Metarsenious acid*,  $\text{HASO}_2$ ; forming *metarsenites*—e.g.,  $\text{NH}_4\text{AsO}_2$ ,  $\text{KAsO}_2$ ,  $\text{Ca}(\text{AsO}_2)_2$ ,  $\text{Pb}(\text{AsO}_2)_2$ , etc. The triad arsenic forms some combination with nearly all metals, but many of its salts are so instable as to prevent the determination of their composition.

**457. Arsenious anhydride**—having both crystalline and amorphous modifications—is very slowly and sparingly soluble in cold water, much more quickly but quite sparingly soluble in hot water, the solution feebly reddening litmus; freely soluble in hydrochloric acid, and somewhat soluble in sulphuric acid without combination; readily soluble in alkali hydroxides with combination, forming, perhaps, the hypothetical  $\text{K}_3\text{AsO}_3$ , but only  $\text{KH}(\text{AsO}_2)_2$ ,  $\text{KAsO}_2$ , and  $\text{K}_4\text{As}_2\text{O}_5$  have been isolated; slightly soluble in alcohol, and soluble in glycerine.—*Arsenious chloride* is wholly decomposed by water, with formation of arsenious oxide and hydrochloric acid (equation a); *arsenious sulphide* is very slightly soluble in pure water, insoluble in acidulated water, but soluble by combination in solutions of alkalis (b), alkaline carbonates and alkaline sulphides (c), (d) and (e).—*Arsenites* of the alkali metals are soluble in water; of the alkaline earth metals sparingly soluble, of magnesium insoluble; of all other metals, insoluble. The arsenites are decomposed—and, except those of first-group metals, dissolved—by hydrochloric acid, and are decomposed and dissolved by nitric acid, without exception:



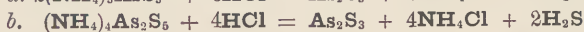
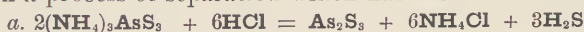
In **analysis**, the second-group precipitate of arsenious sulphide is separated with antimony and tin, by solution with ammonium sulphide. The final determination and separation from antimony is usually effected by the action of the hydrides upon solution of silver nitrate.

**458. Alkali hydrates and carbonates** do not precipitate arsenious compounds from solution; whereby arsenic is distinguished from the bases.

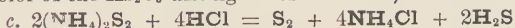
\* Dibasic and monobasic as well as tribasic thioarsenites are formed in different conditions. According to NILSSON (*Bericht. d. deut. chem. Ges.*, IV., 989; *Jour. Chem. Soc.*, X., 1872, 599),  $(\text{NH}_4)\text{HS}$  always dissolves  $\text{As}_2\text{S}_3$  as  $(\text{NH}_4)_2\text{S} \cdot (\text{As}_2\text{S}_3)_2$ . For the action of alkalis and alkaline carbonates upon  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_5$ , and the formation of many thioarsenites and thioarsenates according to NILSSON, see *Jour. prakt. Chem.*, 1876 [2], 14, 1-60 and 145-172.

**459. Hydrosulphuric acid** precipitates the lemon-yellow *arsenious sulphide*,  $\text{As}_2\text{S}_3$ . The precipitate forms promptly in acidulated solutions, the most perfectly with hydrochloric acidulation; being complete even in strong hydrochloric acid solution, but diminished by too strong nitric acid. It forms slowly in simple aqueous solution of arsenious acid, as a color rather than a precipitate; being slightly soluble in pure water, but insoluble in acidulated water. It is not formed in solutions of alkali arsenites, except by acidulation. Citric acid and other *organic* substances hinder, but, in presence of much hydrochloric acid, do not wholly prevent its formation. Alkali **sulphides** produce, and by further addition dissolve, the precipitate.

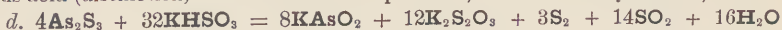
The *arsenious sulphide* is soluble in solutions of alkali hydrates, carbonates, and sulphides, as severally explained in 457. From all these alkaline thioarsenites, acids reprecipitate the sulphide (*a* and *b*). By its solubility in solution of **ammonium sulphide**, it is separated with antimony and tin from the other members of group second; and by its solubility in solution of **ammonium carbonate**, it is approximately separated from antimony and tin, in a process of separation which has been in common use:



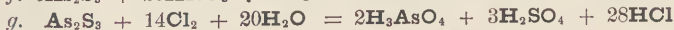
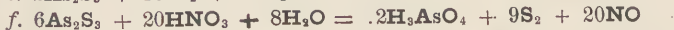
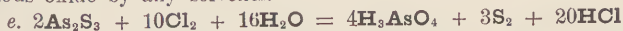
The color of the  $\text{As}_2\text{S}_3$  distinguishes it from **S**, derived thus:



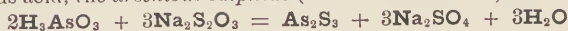
The *arsenious sulphide* is also soluble in solutions of alkali **sulphites** with free sulphurous acid (distinction, and a method of separation, from antimony and tin):



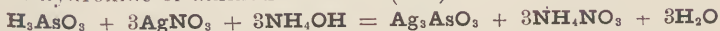
Like metalloidal arsenic, the *arsenious sulphide* is insoluble in **hydrochloric acid**—another means of separation from antimony and tin. It is insoluble in dilute but dissolves in strong **nitric acid**, and by free **chlorine** or nitro-hydrochloric acid, as *arsenic anhydride*,  $\text{As}_2\text{O}_5$ , or arsenic acid,  $\text{H}_3\text{AsO}_4$ —(equations *e* and *f*). Usually, however, a large portion of the **S** is oxidized to  $\text{H}_2\text{SO}_4$ , and completely if the **Cl** or  $\text{HNO}_3$  is used hot and in excess (*g*). Compare equation *a*, 455). Arsenious sulphide is not changed to arsenious oxide by any solvents.



**Thiosulphates**—as  $\text{Na}_2\text{S}_2\text{O}_3$ —also precipitate, from boiling hydrochloric acid solution of arsenious acid, the *arsenious sulphide* (distinction from tin):



**460. Silver nitrate** solution precipitates from neutral solutions of arsenites, or ammonio silver nitrate\* from water solution of arsenious oxide, *silver arsenite*,  $\text{Ag}_3\text{AsO}_3$ , yellow, readily soluble in dilute acids or in ammonium hydroxide or ammonium salts (420):



\* Prepared by adding ammonium hydroxide to the solution of silver nitrate, till the precipitate at first produced is *nearly* all redissolved.

**461. Copper sulphate** solution precipitates from solutions of neutral arsenites, or ammonio copper sulphate (prepared as directed in note under 460) precipitates from water solution of arsenious oxide, the green *copper arsenite*,  $\text{CuHAsO}_3$  (Scheele's green), soluble in ammonium hydroxide and in dilute acids. **Copper acetate** in boiling solution precipitates the green *copper aceto-arsenite*  $(\text{CuOAs}_2\text{O}_3)_3\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  (Schweinfurt green), soluble in ammonium hydroxide and in acids. Both these salts are often designated as Paris green (343). For the reaction of Copper Salts with fixed alkali arsenite, see 475.

**462.** In general, solutions of *arsenites* are precipitated by solutions of normal salts of the metals, except those of the alkalis, and barium, strontium, and calcium (457). Normal magnesium salts form a white precipitate of magnesium arsenite. The precipitate is soluble in ammonium hydroxide and ammonium chloride (distinction from arsenates).

**Ferric** salts precipitate from arsenites, and **recent ferric hydroxide** (*used as an antidote*) forms, with arsenious anhydride, variable *basic ferric arsenites*, scarcely soluble in acetic acid, soluble in hydrochloric acid. Water slowly and sparingly dissolves from the precipitate the arsenious anhydride; but a large excess of the ferric hydroxide holds nearly all the arsenic insoluble. To some extent, the basic ferric arsenites are transposed into basic ferrous arsenates, insoluble in water, in accordance with the reducing power of arsenious oxide.

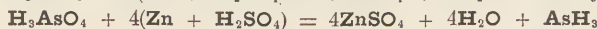
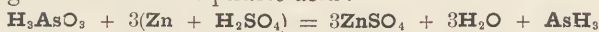
**463.** Arsenic is **reduced** to the elemental state by several methods of great analytical importance.

By the action of **hydrogen** generated in acid solution (MARSH'S METHOD) it is reduced from all its *soluble* compounds, when it enters into a combination with hydrogen as *arsenious hydride*,  $\text{AsH}_3$ , gaseous. The latter can be identified by numerous reactions, and from it the arsenic can readily be obtained free.

The hydrogen is generated by **sulphuric acid** diluted with 6 to 8 parts water, and **zinc** (both free from arsenic). Compare 288. In general *nascent* hydrogen (or any metal with any acid which *produces hydrogen*) gives like results. The hydrogen removes the oxygen, from either oxide of arsenic, by forming water, and then combines with the arsenic; two atoms of hydrogen taking the place of one atom of oxygen:



or, including the zinc and sulphuric acid:



It will be seen that arsenious hydride cannot be formed in presence of free chlorine or other oxidizing agents, such as nitric acid, nitrates, chlorates, and hypochlorites. Sulphides and sulphites interfere; also mercury salts (by amalgamation of the zinc), and *most organic substances*. Arseni-

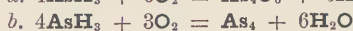


ous sulphides are not acted on by the nascent hydrogen. With zinc, strong **potassium hydroxide** or **sodium hydroxide** may be used instead of acid, the action being slower ; but quite rapid if finely divided iron, platinum, or some other metals are present. **Sodium amalgam** alone, in solutions neutral, acid, or alkaline, causes an abundant generation of arsenious hydride if arsenic is present. In the test made by sodium amalgam, in alkaline solution, cane sugar and some other organic bodies do not interfere.

The generation of arsenious hydride, by metallic **magnesium**, when done in strong solution of **ammonium chloride**, is a separation from antimony. The solution may be neutral or alkaline, but, for the separation, not acid.

Metallic **aluminium**, in strong potassium hydroxide solution, on warming, generates arsenious hydride from arsenical compounds (distinction and separation from antimony).

**464.** *Arsenious hydride* (arsine) burns when a stream of it is ignited where it enters the air, and explodes when its mixture with air is ignited, like other combustible gases. It burns in a stream, with a somewhat luminous and slightly bluish flame (distinction from hydrogen) ; the hydrogen being first oxidized, and the liberated arsenic becoming incandescent, and then undergoing oxidation ; the vapors of water and arsenious anhydride passing into the air (*a*). If a piece of **cold porcelain** is held in the flame, the reduction of temperature prevents the oxidation of the arsenic, which is deposited in dark steel-gray *spots*, adherent to the porcelain, about which a little of the water of combustion condenses (*b*) :



In many particulars above mentioned, the combustion of arsenious hydride resembles that of the hydrocarbons of illuminating gas.

Arsenious hydride is an exceedingly poisonous substance, the inhalation of the un-mixed gas being quickly fatal. Its dissemination in the air of the laboratory, even in the small portions which are not appreciably poisonous, should be avoided. Furthermore, as it is recognized or determined, in its various analytical reactions, only by its decomposition, to permit it to escape undecomposed is so far to fail in the object of its production. The evolved gas should be constantly run into silver nitrate solution, or kept burning.

**465.** Arsenious hydride is decomposed by **heat** alone. In passing through glass tubes, heated to incipient redness, the gas is decomposed, the arsenic adhering to the inner surface of the tube, beyond the heated part, as a steel-gray *mirror coating*. This coating is readily driven by the heat, is gradually dissipated by hot hydrogen gas, and imparts the garlic odor to the escaping hydrogen gas. The latter, if ignited, will generally deposit arsenic spots on porcelain, showing that the arsenic is not wholly retained in the tube.

**466.** Both the *mirror* and the *spots* exhibit the properties of free arsenic (455). Liquid reagents are most convenient for application to the spots. The reactions of these deposits having analytical interest are such as distinguish arsenic from antimony.



## Comparison of Arsenic and Antimony, deposited from $\text{AsH}_3$ and $\text{SbH}_3$ .

### Arsenic Spots.

Of a steel gray to black *lustre*.

*Volatile* at  $450^\circ \text{C}$ .; as arsenious acid, at  $218^\circ \text{C}$ .

Dissolve in *hypochlorite* (a).

Warmed with a drop of *ammonium sulphide*, form yellow spots (459), soluble in *ammonium carbonate*, insoluble in *hydrochloric acid*.

With a drop of hot nitric acid, dissolve clear (455)

The clear solution, with a drop of solution of *silver nitrate*, when treated with vapor of ammonia (from a glass rod moistened with ammonium hydrate and held near), gives a brick-red or a yellow color (391).

With vapor of *iodine*, color yellow, by formation of arsenious iodide, readily volatile when heated.

### Arsenic Mirror.

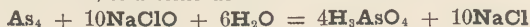
Deposited *beyond* the flame; the gas being decomposed by a red heat (465).

The mirror is *driven* at  $450^\circ \text{C}$ .; it does not melt.

By vaporization in the stream of gas, escapes with a garlic *odor*.

By slow vaporization in a current of air (the tube open at both ends and held inclined over the heat), a deposit of octahedral *crystals* is obtained above—if abundant, forming a white coating (457), soluble in water, the solution giving reactions for arsenic.

a. The **hypochlorite** reagent—usually  $\text{NaClO}$ —decomposes in the air and light, by keeping. It should instantly and perfectly bleach litmus-paper (not reddened it). It dissolves arsenic by oxidation, to arsenic acid:



467. When arsenious hydride is passed into solution of **silver nitrate**, the silver is reduced to metal by the oxidation of both elements in the gas—the hydrogen to water, and the arsenic to arsenious acid, which remains in solution along with the liberated nitric acid (distinction from antimonious hydride, which precipitates antimonious argentide):



### Antimony Spots.

Of a velvety brown to black surface.

Volatile in vacuo at white heat; by oxidation, at a red heat.

Do not dissolve in hypochlorite.

Warmed with ammonium sulphide, form orange-yellow spots, insoluble in ammonium carbonate, soluble in hydrochloric acid.

With a drop of hot dilute nitric acid, turn white.

The white fleck, treated with silver nitrate and vapor of ammonia, gives no color until warmed with a drop of ammonium hydrate, then gives a black color.

With vapor of iodine, color more or less carmine red, by formation of antimonious iodide, not readily volatile by heat.

### Antimony Mirror.

Deposited *before* or on both sides of the flame; the gas being decomposed considerably below a red heat.

The mirror melts to minute globules at  $432^\circ \text{C}$ ., and then is driven at a red heat.

The vapor has no odor.

By vaporization in a current of air, a white amorphous coating is obtained—insoluble in water, soluble in hydrochloric acid, and giving reactions for antimony.

The *reactions for the arsenious oxide* formed in solution should be obtained after filtering out the brown-black precipitate of silver, then adding a very little hydrochloric acid, that the silver in the undecomposed nitrate may be removed as chloride. From the filtrate, hydrosulphuric acid precipitates the sulphide, and arsenic may be quantitatively determined from the weight of this precipitate, after Marsh's Test. Reliance should not be placed on blackening of the silver nitrate alone, as this may be due to  $\text{SbH}_3$ , or to  $\text{H}_2\text{S}$  or to  $\text{PH}_3$ .  $\text{H}_2\text{S}$  would be generated in the test, from sulphides; and  $\text{PH}_3$  from hypophosphites or phosphites.

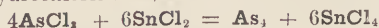
If the material treated with zinc and dilute sulphuric acid be placed in a flask or large test-tube, and a paper moistened with silver nitrate be tied over the mouth, it will (on standing) be blackened by arsenious hydride. The interference of hydrosulphuric acid may be avoided by causing the gas to pass through cotton-wool, moistened with solution of lead acetate, and carefully placed to fill the neck of the vessel, then left several hours. This operation may be relied on for negative results, in testing the purity of reagents, etc.

The yellow *silver arsenite* (460) may be obtained as a distinctive test, with the silver nitrate left in solution, undecomposed by the arsenious hydride, after filtering out only the metallic silver, by the careful addition of ammonium hydroxide, in repeated small portions, by the glass rod, till the nitric acid and arsenious anhydride are just neutralized:



Arsenious hydride received in **nitric acid** is changed to  $\text{H}_3\text{AsO}_4$ , soluble in water (separation from antimony).

**468. Stannous chloride,  $\text{SnCl}_2$ , reduces** arsenious and arsenic oxides, from hot concentrated hydrochloric acid solution, as flocculent, black-brown, metalloidal *arsenic*, containing three or four per cent. of tin (BETTENDORF'S METHOD). The arsenic, in solution with the concentrated hydrochloric acid, *acts* as arsenious chloride (457 a):



The hydrochloric acid should be 25 to 33 per cent.; if not over 15 to 20 per cent., the reaction is slow and imperfect. Sulphuric acid with sodium chloride may be taken instead of hydrochloric acid:

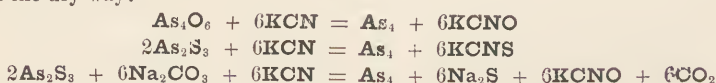
In a wide test-tube place 0.1 to 0.2 gram. (2 or 3 grains) of the (oxidized) solid or solution to be tested, add about 1 gram. (15 grains) of *sodium chloride*, and 2 or 3 cub. centim. (about one fluid drachm) of *sulphuric acid*, then about 1 gram. (15 grains) of crystallized *stannous chloride*; agitate, and heat to boiling several times, and set aside for a few minutes. Traces of arsenic give only a brown color; notable proportions give the flocculent precipitate. A dark-gray precipitate may be due to mercury (448 a), capable of being gathered into globules. If a precipitate or a darkening occurs, obtain conclusive evidence whether it contains arsenic or not, as follows: Dilute the mixture with ten to fifteen volumes of about 12 per cent. hydrochloric acid (equal parts of Fresenius's Reagent and water); set aside, decant; gather the precipitate in a wet filter, wash it with a mixture of hydrochloric acid and *alcohol*, then with alcohol, then with a little ether, and dry in a warm place. A portion of this dry precipitate is now dropped into a small hard-glass tube, drawn out and closed at one end, and heated in the flame: *arsenic* is identified by its mirror (466), easily distinguished from mercury (449). *Antimony* is not reduced by stannous chloride; other reducible metals give no mirror in the

reduction-tube. Small proportions of organic material impair the delicacy of this reaction, but do not prevent it. It is especially applicable to the hydrochloric acid distillate, obtained in separation of arsenic, according to 474.

**469.** Metallic **copper** reduces arsenious oxide, from hydrochloric acid solution, as an iron-gray film or crust of *arsenic with copper*, 32 per cent. arsenic, or  $\text{Cu}_3\text{As}_2$  (REINSCH'S METHOD). The copper should be in bright strips, the solution hot, and the reaction awaited for some time. If much arsenic is present, the crust peels off in black scales. The crusts are not evidence of arsenic without further examination—according to 470, etc.—as antimony, silver, and other metals are reducible by copper. The film may be obtained and afterwards determined as arsenic, when but the 0.0005 gram\* is taken in pure hydrochloric acid solution.

**470.** In Marsh's Test, a portion of the arsenic, reduced by the **zinc** to the elemental state, remains for a short time, while the arsenic is in excess in the solution, as a grayish-black film upon the zinc. If the generation of hydrogen be continued after the arsenic is all reduced, all the latter soon forms arsenious hydride. The deposition of antimony, in Marsh's Test, is much greater than that of arsenic. Also, if the operation be conducted in a platinum vessel or with platinum foil, in contact with the zinc, the reduced arsenic does not adhere to the platinum as firmly as the reduced antimony.

**471.** **Potassium cyanide**, with sodium carbonate, reduces arsenic from all its compounds, in the dry way:



If this reduction be performed in a small reduction-tube with a bulb at the end, the reduced arsenic sublimes and condenses as a mirror (466) in the cool part of the tube. The presence of compounds of manganese, bismuth, zinc, or antimony hinders this reaction, but does not prevent it. The test can be performed in presence of mercury compounds, but more conveniently after their removal; in presence of organic material, it is altogether unreliable. If much free *sulphur* is present, H. Rose recommends that the arsenic should be removed from it, by dissolving in ammonia, evaporating the solution to dryness, oxidizing to arsenic acid with hydrochloric acid and potassium chlorate (475), precipitating with ammonium hydroxide and magnesium solution as arsenate (478), and washing and drying the latter for the test.

The thoroughly dried substance is mixed with six times its bulk of a dry mixture of equal parts of anhydrous sodium carbonate and potassium cyanide, and introduced into the bulb of the reduction-tube, which should not be over half filled. Heat the bulb very gently over the flame, and if water rises and condenses in the tube, thoroughly dry the bulb and tube—wiping the inside of the tube with twisted paper. Then heat strongly, while the tube is held inclined, finally to a full red heat. If arsenic is present, the *mirror* will be seen above the bulb, and can be tested, as stated in 466, etc.

This operation becomes a more delicate test, and excludes antimony from the mirror, if the mixture be placed in a larger horizontal reduction-tube, drawn out narrow at one end, and connected at the other with an apparatus for generating and drying carbonic anhydride, which is passed over the substance during the reduction (METHOD OF FRESE-

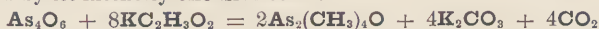
NIUS AND BABO): Three parts of anhydrous sodium carbonate, with one of potassium cyanide, are taken, and ten or twelve parts of this mixture to one part of the substance tested, the whole well mixed and thoroughly dried (in the water-oven). The reduction-tube should be about 1.25 centimeters (one-half inch) wide and 10 to 15 centimeters (four to six inches) long, besides the drawn-out part. At the end not drawn out it is connected with a small wash-bottle, for sulphuric acid, and this connected with the flask for generating carbonic anhydride with marble and dilute hydrochloric acid. The dried mixture is introduced in the middle of the reduction-tube, by aid of a paper gutter; the connections made, and the substance again dried by gentle heat. When the atmosphere is expelled and a steady stream of carbonic anhydride is passing through the apparatus, heat the tube between the mixture and the drawn-out end to redness, and then heat the mixture gradually to redness of the tube, driving the mirror to the narrowed portion of the tube. Finally, detach the tube, close the small end in the flame, and advance the heat up to the mirror.

**472.** Charcoal reduces arsenious oxide very readily, by heat in the glass tube. A small hard-glass tube is drawn out at one end, the extremity closed in the flame, and a particle of the well-dried material dropped into the tube, so that it will fall to the end of the narrow part. A fragment of recently burned charcoal is pushed down nearly to the substance, and heat applied, first to the charcoal and then to the substance, to redness. The mirror forms just above the heated part, and may farther be tested as stated in 466. During the reduction, the garlic odor is observed.

All compounds of arsenic, heated with sodium carbonate on charcoal, and all oxidized compounds heated on charcoal alone, present the odor of arsenic.

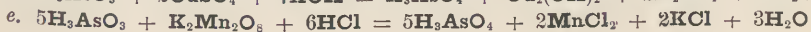
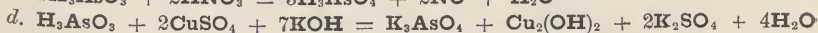
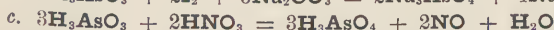
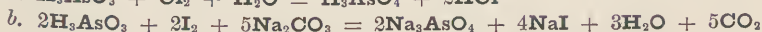
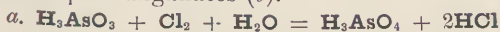
Non-oxidized forms of arsenic, heated in air, as in a glass tube open at both ends, oxidize to arsenious anhydride (455); and the latter substance sublimes in the tube, producing a white coating of microscopic octahedral crystals.

**473.** If dry arsenious anhydride is heated with dried sodium acetate, in the bulb of a small reduction-tube, *arsen-dimethyl oxide*, or cacodyl oxide,  $\text{As}_2(\text{CH}_3)_4\text{O}$ , is produced and recognized by its intensely offensive odor:



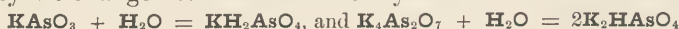
**474.** Arsenic is removed from mixture with metallic salts and non-volatile acids, and obtained in a concentrated form, by distilling the mixture with concentrated hydrochloric acid—or sodium chloride and sulphuric acid—when *arsenious chloride* passes over at  $132^\circ \text{C}$ . ( $270^\circ \text{F}$ .) and condenses with hydrochloric acid. A flask over a sand-bath, with a tube passing through the stopper and then inclined downwards to a small receiving flask set in a vessel of cold water, constitutes a sufficient apparatus. The distillate may be examined according to 468.

**475.** Arsenious compounds are oxidized to arsenic compounds by a large number of oxidizing agents. As already stated (455 and 459 *e, f*), the solvents of elemental arsenic, and of arsenious sulphide, produce pentad arsenic compounds. Among the oxidations of arsenious compounds most used in analysis are those by action of chlorine or bromine (*a*), iodine with sodium carbonate (*b*), nitric acid (*c*), copper sulphate with free fixed alkali (*d*), and permanganates (*e*).





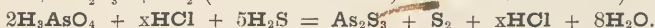
**476. ARSENIC OXIDE AND ACIDS.**— $\text{As}_2\text{O}_3$  is not produced by heating  $\text{As}$  or  $\text{As}_4\text{O}_6$  in the air or in oxygen gas. But when  $\text{As}$  or  $\text{As}_4\text{O}_6$  is treated with  $\text{Cl}$  or  $\text{HNO}_3$  *orthoarsenic acid* ( $\text{H}_3\text{AsO}_4$ ) is produced; and when this is heated at  $140^\circ$  to  $180^\circ$  C. *pyroarsenic acid* ( $\text{H}_4\text{As}_2\text{O}_7$ ) is formed; and when the heat is increased to  $200^\circ$  C. *metarsenic acid*,  $\text{HAsO}_3$ , is produced; and at a dull red heat *arsenic oxide—arsenic anhydride*—( $\text{As}_2\text{O}_3$ ) is formed; and at still higher temperatures oxygen is given off and  $\text{As}_2\text{O}_3$  sublimes. Each acid forms corresponding salts: *metarsenates* ( $\text{M}'\text{AsO}_3$ ); *pyroarsenates* ( $\text{M}'_4\text{As}_2\text{O}_7$ ); *orthoarsenates* ( $\text{M}'_3\text{AsO}_4$ ). There are three classes of the latter,  $\text{M}'_3\text{AsO}_4$ ,  $\text{M}'_2\text{HAsO}_4$ , and  $\text{M}'\text{H}_2\text{AsO}_4$ . Arsenic anhydride, *meta* and *pyroarsenic acids*, are known only in a solid state, being changed by water to *orthoarsenic acid*. Their salts have not been much investigated. As a rule, they are changed to orthoarsenates by water.



The *arsenates* of the alkali metals are all *soluble* in water; only the mono-metallic arsenates of the other metals are soluble in water, but their di- and tri-metallic arsenates are soluble in arsenic acid (as mono-metallic salts) and in the stronger mineral acids (by decomposition). In acetic acid they dissolve with more or less difficulty; many of them are soluble in solutions of ammonium salts.

In *analysis*, the formation of arsenious hydride occurs alike with pentad and triad arsenic. For distinctions from arsenious compounds, see 488.

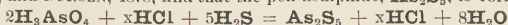
**477. Hydrosulphuric acid** precipitates, very tardily, in solutions of arsenic acid or acidulated arsenates, the yellow *arsenious sulphide*, with free sulphur,  $\text{As}_2\text{S}_3 + \text{S}_2$  (WACKENRODER, LUDWIG, H. ROSE).



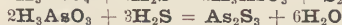
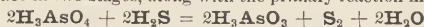
In the cold, addition of solution of hydrosulphuric acid causes no appreciable immediate effect (distinction from arsenious acid); but, by treatment with the gas for 12 to 24 hours, better at about  $70^\circ$  C. ( $160^\circ$  F.), all the arsenic can be thrown down. Also, more readily, by previous reduction, according to 484. The precipitate has the properties stated in 457 and 459, with the additional properties of free sulphur, which in its recent condition is taken up by alkali hydroxides or by carbon disulphide.\*

**Ammonium sulphide** precipitates solutions of arsenic acid, more

\* BERZELIUS, 1826, and BUNSEN, 1878, find that the pentasulphide,  $\text{As}_2\text{S}_5$ , is formed,



B. BRAUNER and F. TOMICEK (*Jour. Chem. Soc.*, 1888, 53, 145) find that the formation of the pentasulphide is favored by a *larger* quantity of  $\text{HCl}$  and a *larger* quantity of  $\text{H}_2\text{S}$  and by a *lower temperature*; and the formation of the trisulphide is favored by a *smaller* amount of  $\text{HCl}$  and a *smaller* amount of  $\text{H}_2\text{S}$  and a *higher temperature*; and "when a *rapid current* of  $\text{H}_2\text{S}$  is passed into a solution of arsenic acid,  $\text{As}_2\text{S}_5$  alone is formed, although but slowly, if free  $\text{HCl}$  is present, and the liquid is kept warm. And when the gas is *passed slowly* into a solution of the free acid, or into warm acid solutions of arsenates, a secondary reaction takes place in two stages, along with the primary reaction mentioned above—



For quantitative estimation of arsenic acid in the form of a sulphide it is best to convert it into  $\text{As}_2\text{S}_5$ , and for this purpose BUNSEN's method must be *strictly adhered to*."



rapidly than is done by hydrosulphuric acid, as *arsenic sulphide*,  $\text{As}_2\text{S}_5$ —readily soluble in excess of the reagent, as ammonium thioarsenate,  $(\text{NH}_4)_3\text{AsS}_4$ .

**Thiosulphates** react as with arsenious compounds (459), free sulphur being separated.

When the precipitate of  $\text{As}_2\text{S}_3 + \text{S}_2$  is dissolved by alkali sulphides, thioarsenates are formed, as  $\text{K}_3\text{AsS}_4$ , potassium orthothioarsenate,  $\text{K}_4\text{As}_2\text{S}_7$ , potassium pyrothioarsenate, and  $\text{NH}_4\text{AsS}_3$ , potassium metathioarsenate. Thus :



Dilute ammonium hydroxide, and ammonium carbonate, however, dissolve the arsenious sulphide as thioarsenite and arsenite, leaving the free sulphur undissolved.

**478. Magnesium salts** with ammonium chloride, and free ammonium hydroxide, precipitate *ammonium-magnesium arsenate*,  $\text{MgNH}_4\text{AsO}_4$ , white, easily soluble in acids (distinction from arsenites). The reagents should be first mixed together, and used in a clear solution—"the magnesium mixture"—to make sure that enough ammonium salt is present to prevent the precipitation of magnesium hydroxide by the ammonium hydroxide. The precipitate forms slowly and with crystallization, but completely. Compare with the corresponding ammonium magnesium phosphate (79).

**479. Solution of barium hydroxide** precipitates solution of arsenic acid partially, and solution of alkali arsenates almost completely, as *barium arsenate*,  $\text{BaHAsO}_4$ , from dimetallic solutions, and  $\text{Ba}_3(\text{AsO}_4)_2$  from mono-metallic. The precipitate is sparingly soluble in water. If **ammonium hydroxide** is added with the baryta, the *ammonium-barium arsenate*,  $\text{BaNH}_4\text{AsO}_4$ , is precipitated, insoluble in water, and not made soluble by ammonium salts or by ammonium hydroxide (distinction from arsenites).

The tri- and di-metallic *calcium* arsenates are insoluble in water; the ammonium calcium arsenate,  $\text{CaNH}_4\text{AsO}_4$ , is sparingly soluble.

**480. Salts of the third and second group metals** precipitate solutions of arsenic acid but slightly, but precipitate solutions of tri-metallic and di-metallic alkali arsenates completely (as, respectively, tri-metallic and di-metallic arsenates)—in accordance with the solubilities of arsenates stated in 475.

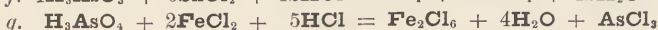
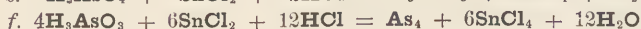
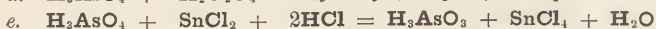
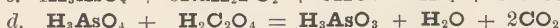
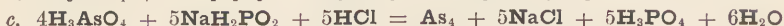
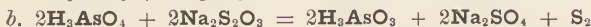
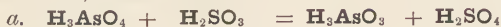
**481. Silver nitrate** solution precipitates neutralized arsenic acid as *silver arsenate*,  $\text{Ag}_3\text{AsO}_4$ , reddish-brown; the solubilities and conditions of precipitation being the same as for the arsenite (460).

**Copper sulphate** solution precipitates solutions of arsenates as *copper arsenate*,  $\text{CuHAsO}_4$ , greenish-blue, the solubilities and conditions of precipitation being the same as for the arsenites (461).

**482. Ferric salts**, with alkali acetates, precipitate, from solution of arsenic acid, or from acidulated solution of arsenates, *ferric arsenate*,  $\text{Fe}_2(\text{AsO}_4)_2$ , yellowish-white, insoluble in acetic acid (compare equation in 216). Ferric salts alone precipitate, from dimetallic arsenates, two-thirds metallic ferric arsenate,  $\text{Fe}_2\text{H}_3(\text{AsO}_4)_3$ .

**483. Ammonium Molybdate**,  $(\text{NH}_4)_2\text{MoO}_4$ , in nitric acid solution, gives a yellow precipitate of *ammonium arsenio-molybdate*, of variable composition. Compare Phosphomolybdates.

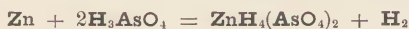
**484. Reducing agents** change arsenic compounds either into arsenious compounds only, or into elemental arsenic. Sulphurous acid and sulphites (*a*), thiosulphates (*b*), hypophosphites (*c*), oxalic acid (*d*), stannous salts (*e*) and (*f*), and ferrous salts in concentrated hydrochloric acid solution at 132° C. (*g*), reduce arsenic acid to arsenious acid without further change; also, the precipitation of arsenic acid as arsenious sulphide involves reduction by **hydrosulphuric acid**—a reduction precisely corresponding to that of ferric salts in their precipitation as ferrous sulphide. For the study of reductions of pentad arsenic, see 490 and Part II.



**485.** By reaction *g*, of the preceding paragraph, we are enabled to remove the arsenic in arsenic acid, from mixture of non-volatile inorganic salts and acids, by **distillation of arsenious chloride**—as directed for arsenious acid, in paragraph 474. In presence of water, neither heat with hydrochloric acid alone, nor ferrous salts without heat, convert arsenic acid to arsenious chloride. The hydrochloric acid should be as strong as 25 per cent.; otherwise, sodium chloride and concentrated sulphuric acid should be used instead.

**486.** Arsenic acid vaporizes by decomposition at a low red heat (as stated in 476); but, in absence of reducing agents, the arsenates of the alkali metals bear **full ignition** without change. In the removal of organic matter by combustion, excess of potassium nitrate must be added to counteract the reducing influence of the carbon. After fusion as sodium arsenate, antimony is separated by insolubility, according to the plan given under antimony.

**487.** The **reducing agents** which separate metalloidal arsenic from *arsenious compounds*, effect the same result with arsenic acid, though not quite so readily. The analytical methods described in 463 to 475, inclusive, have all been given for arsenious and arsenic oxides alike. In solution of arsenic acid in water, *without other acid*, **zinc** and other metals do not effect reduction, but are dissolved as acid arsenates with evolution of hydrogen:



**488.** The reactions *distinguishing between arsenious and arsenic acids* have been described: action of arsenious acid as a reducing agent, 475; the precipitation of ammonium earth-metal arsenates, 478; of arsenio-molybdate, 483; the slow precipitation of arsenic acid by hydrosulphuric acid, 477; the colors of the silver salts, 460 and 481, and of the copper salts, 461 and 481.

**489. Estimation.**—(1) As  $\text{Pb}_3(\text{AsO}_4)_2$ . To a weighed portion of the solution, containing arsenic acid, a weighed amount of **PbO** is added. After evaporation and ignition at a dull red heat it is weighed as  $\text{Pb}_3(\text{AsO}_4)_2$ . The weight of the added **PbO** is subtracted from the residue, and the difference shows the amount of arsenic present reckoned as  $\text{As}_2\text{O}_5$ . (2) It is precipitated by **MgSO<sub>4</sub>** in presence of **NH<sub>4</sub>OH** and **NH<sub>4</sub>Cl**, and after dry-

ing at  $103^{\circ}$  C. weighed as  $\text{MgNH}_4\text{AsO}_4 + \text{H}_2\text{O}$ . (3) The  $\text{MgNH}_4\text{AsO}_4$  is converted by ignition into  $\text{Mg}_2\text{As}_2\text{O}_7$ , and weighed. (4) The solution of arsenious acid containing  $\text{HCl}$  is precipitated by  $\text{H}_2\text{S}$ , and the excess of  $\text{H}_2\text{S}$  removed by  $\text{CO}_2$ ; and after removal of the free sulphur, if any is present, by  $\text{CS}_2$ , the precipitate is weighed as  $\text{As}_2\text{S}_3$ . (5) Uranyl acetate, in presence of ammonium salts, precipitates  $\text{NH}_4\text{UO}_2\text{AsO}_4$ ; by ignition this is converted into uranyl pyroarsenate  $(\text{UO}_2)_2\text{As}_2\text{O}_7$ , and weighed as such. (6) Volumetrically:  $\text{As}'''$  is converted into  $\text{As}^v$  by a graduated solution of  $\text{I}$  in presence of  $\text{NaHCO}_3$ . The end of the reaction is shown by its giving a blue color to starch. (7)  $\text{As}'''$  is oxidized to  $\text{As}^v$  by a graduated solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ , and the excess of  $\text{K}_2\text{Cr}_2\text{O}_7$  determined by a graduated solution of  $\text{FeSO}_4$ . (8)  $\text{As}'''$  is converted into  $\text{As}^v$  by a weighed quantity of  $\text{K}_2\text{Cr}_2\text{O}_7$  with  $\text{HCl}$ , and determining the excess of  $\text{Cl}$  by  $\text{KI}$  and  $\text{Na}_2\text{S}_2\text{O}_3$ . Very many other volumetric methods have been recommended.

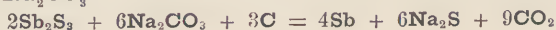
**490. Oxidation.**— $\text{As}^v$  and  $\text{As}'''$  are reduced to metallic arsenic ( $\text{As}^0$ ) by fusion with  $\text{CO}$ , with free carbon or combined as  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{HCN}$ , etc. By  $\text{SnCl}_2$  and  $\text{H}_3\text{PO}_2$  in strong  $\text{HCl}$  solution; also with greater or less completeness by some free metals, such as  $\text{Cu}$ ,  $\text{Cd}$ ,  $\text{Zn}$ , etc.; and in presence of any free acid which will generate hydrogen with the metal the arsenic is still further reduced to  $\text{As}''''\text{H}_3$ . In solution  $\text{As}^v$  is reduced to  $\text{As}'''$  by  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{H}_3\text{PO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{HI}$ ,  $\text{HCNS}$ , etc. Arsenious hydride ( $\text{As}''''\text{H}_3$ ) is oxidized to  $\text{As}'''$  by  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HIO}_3$ , and to  $\text{As}^v$  by  $\text{HNO}_2$ ,  $\text{HNO}_3$ ,  $\text{Cl}$ , and  $\text{Br}$  (II. B. PARSONS, *Chem. News*, 35, 235).  $\text{As}'''$  is oxidized to  $\text{As}^v$  by  $\text{HNO}_3$ ,  $\text{Cl}$ ,  $\text{HClO}$ ,  $\text{HClO}_3$ ,  $\text{Br}$ ,  $\text{HBrO}_3$ , and  $\text{HIO}_3$ ; also in the presence of an acid, such as dilute  $\text{H}_2\text{SO}_4$ , by  $\text{PbO}_2$ ,  $\text{H}_2\text{CrO}_4$ , and by compounds of  $\text{Co}$ ,  $\text{Ni}$ , and  $\text{Mn}$  which have more than two bonds; and in alkaline mixture by  $\text{I}$ ,  $\text{PbO}_2$ ,  $\text{Ag}_2\text{O}$ ,  $\text{Hg}_2\text{O}$ ,  $\text{HgO}$ ,  $\text{CuO}$ ,  $\text{K}_2\text{CrO}_4$ , etc. See also Part II.

## ANTIMONY. $\text{Sb} = 119.955$ .

**491. Specific gravity**, 6.697 (SCHRÖDER, 1859). *Melting point*,  $432^{\circ}$  C. ( $809^{\circ}$  F.) (CARNELLEY and WILLIAMS, 1879). Valence, a pentad in  $\text{Sb}^v_2\text{O}_5$ , and a triad in  $\text{Sb}'''_4\text{O}_6$ . According to *oxidation valence*, it is zero in metallic antimony ( $\text{Sb}^0$ ); and in antimonious hydride it is a negative triad ( $\text{Sb}''''\text{H}_3$ ).

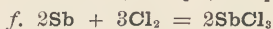
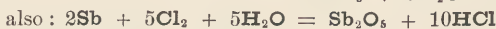
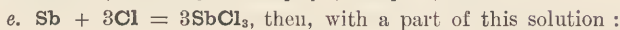
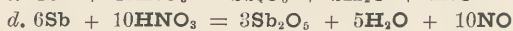
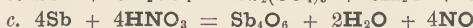
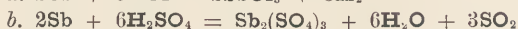
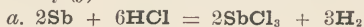
**492. Occurrence.**—Found native, but more commonly as stibnite ( $\text{Sb}_2\text{S}_3$ ). Also found as valentinite,  $\text{Sb}_2\text{O}_3$ . And in very many minerals usually combined with other metals as a double sulphide.

**493. Preparation.**—The ore is converted into the oxide by roasting, and then reduced by fusion with carbon. (2) The sulphide is fused with charcoal and  $\text{Na}_2\text{CO}_3$ :



(3) It is reduced by metallic iron,  $\text{Sb}_2\text{S}_3 + 3\text{Fe} = 2\text{Sb} + 3\text{FeS}$ . To separate it from other metals with which it is frequently combined requires a special process, according to the nature of the ore.

**494. Properties.**—A lustrous, bluish-white, brittle, and readily pulverizable metal, fusible at  $432^\circ \text{C}$ , and slowly volatile at a white heat.—It is but little tarnished in dry air; in moist air it oxidizes slightly, with formation of a blackish-gray mixture of metal and antimonious oxide; when melted, it oxidizes quickly, and at a red heat it burns with a white light, and white, inodorous vapors—the formation of the antimonious oxide,  $\text{Sb}_2\text{O}_3$ .—Boiling concentrated hydrochloric acid slowly dissolves powdered antimony (*a*), but when in the compact state it resists that acid; boiling concentrated sulphuric acid slowly converts it into antimonious sulphate with evolution of sulphurous anhydride (*b*); nitric acid rapidly oxidizes it, the dilute acid forming chiefly antimonious oxide (*c*), the concentrated forming mostly  $\text{Sb}_2\text{O}_5$  and antimonie anhydride (*d*)—these oxides being insoluble in the dilute, slightly soluble in the concentrated acid; nitro-hydrochloric acid rapidly converts the metal into soluble antimonious chloride and insoluble oxides (*e*); but if the nitric acid be added to the hydrochloric acid in very small portions during the solution, only the antimonious chloride is formed (*f*).  $\text{SbCl}_5$  is formed by distilling  $\text{SbCl}_3$  in a stream of dry chlorine. Boiling solution of tartaric acid slowly dissolves precipitated antimony (*g*). Alkalies do not dissolve it.



**495. Oxides.**—Antimony forms three oxides— $\text{Sb}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$ , and  $\text{Sb}_2\text{O}_4$ . Antimonious oxide ( $\text{Sb}_2\text{O}_3$ ) is formed (1) by the action of dilute  $\text{HNO}_3$  upon  $\text{Sb}$ ; (2) by precipitating  $\text{SbCl}_3$  with  $\text{Na}_2\text{CO}_3$  or by  $\text{NH}_4\text{OH}$ ; (3) by dissolving  $\text{Sb}$  in concentrated  $\text{H}_2\text{SO}_4$  and precipitating with  $\text{Na}_2\text{CO}_3$ . Its vapor density is 286.5. Hence the molecule is supposed to be  $\text{Sb}_4\text{O}_6$ , not  $\text{Sb}_2\text{O}_3$  (V. and C. MEYER, 1879).  $\text{Sb}'''$  sometimes acts as an acid, but more commonly as a base. Antimonie oxide ( $\text{Sb}_2\text{O}_5$ ) is formed by treating  $\text{Sb}$ ,  $\text{Sb}_4\text{O}_6$ , or  $\text{Sb}_2\text{O}_4$  with concentrated nitric acid. A diantimony tetroxide ( $\text{Sb}_2\text{O}_4$ ) is formed when  $\text{Sb}$  or its other oxides are heated in oxygen or in the air, the triad gaining oxygen and the pentad losing it. The antimony in this compound is probably not a tetrad, but a chemical union of the triad and the pentad :



**496. Reactions of Antimonious Salts.**—Antimonious oxide is slightly soluble in water, insoluble in alcohol; freely soluble, by full or partial combination, in aqueous solutions of tartaric (*a*), hydrochloric (*b*), and other

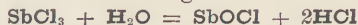


acids, not in nitric acid; soluble in strong solutions of alkalis. The *chloride* is very deliquescent, and freely soluble in water acidulated with hydrochloric acid or with tartaric or citric acid, soluble in aqueous solution of sodium chloride, and soluble in alcohol. The *bromide* requires tolerably concentrated hydrobromic, and the *iodide* quite concentrated hydriodic acid, for solution. The *sulphates* require moderately concentrated sulphuric acid for solution (compare 326; and see, further, 497). The *tartrate* is soluble in water without acidulation; the potassium antimonious tartrate, soluble in water and in glycerine, insoluble in alcohol.

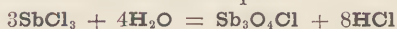


In **analysis**, antimony sulphide is separated, with arsenic and tin sulphides, from other second-group precipitates, by solution in ammonium sulphide. The separation from arsenic and tin is effected through antimonious hydride (504 and 506).

**497. Water** decomposes the acidulated solutions of antimonious salts, with precipitation of a portion as *basic salt*, and the separation of acid, which, restoring the acid strength lost by dilution with the water, holds the other portion of the original salt in solution. In solution of the chloride,  $\text{SbCl}_3$ , the basic salt precipitated by water is the white antimonious oxychloride,  $\text{SbOCl}$ , “Powder of Algaroth”:



The composition of the precipitate is variable, however, each addition of water removing more hydrochloric acid, and leaving the precipitate nearer to the normal oxide. For example:



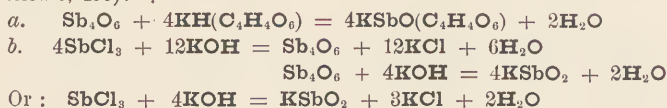
The precipitate is soluble in tartaric acid (distinction from bismuth, 358). In presence of sufficient tartaric or citric acid, water does not decompose antimonious chloride; the *tartrates* of antimony, and of antimony and potassium, being dissolved by water without decomposition. The water solution of tartrate is liable to precipitation of basic salt by *hydrochloric*, sulphuric, and nitric acids.

**498. Solutions of the fixed alkali hydroxides** precipitate, from the acidulated solution of antimonious chloride or of other inorganic antimonious salt, in absence of tartaric and citric acids, the white and bulky *antimonious oxide*,  $\text{Sb}_2\text{O}_3$ , quite readily soluble in excess of the reagents, more quickly by heating; soluble in solution of fixed alkali carbonates when heated, but scarcely at all in the cold; insoluble in ammonium hydroxide. The precipitate is slightly soluble in water, and becomes crystalline after warming, if no alkali hydroxide is present. It dissolves readily in solution of tartaric acid (496 *a*), also in that of potassium hydrogenn tartrate (*a*).

The solution of antimonious oxide by alkalis is due to its combination with them, acting as a feebly acidulous anhydride and forming *antimonites*, which are found to be

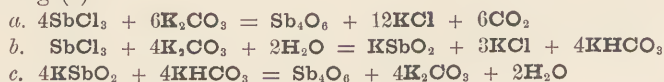


monobasic, so far as capable of isolation (*b*). Sodium antimonite,  $\text{NaSbO}_2$ , is the most stable and least soluble in water; potassium antimonite,  $\text{KSbO}_2$ , is freely soluble in dilute potassium hydroxide solution, but decomposed by pure water. By long standing (24 hours), a portion of the antimonious oxide deposits from the alkaline solution, and the presence of alkali hydrogen carbonates causes a nearly complete separation of that oxide (equation *c*, 499):



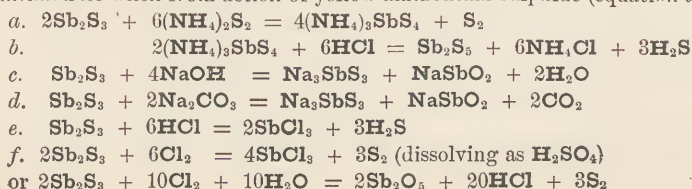
Ammonium hydroxide gives the same precipitate,  $\text{Sb}_2\text{O}_3$ , scarcely at all soluble in excess.

499. The alkali carbonates likewise precipitate *antimonious oxide* (*a*), soluble in a strong excess of the fixed alkali carbonates when warmed (*b*) (distinction from tin); insoluble in excess of ammonium carbonate. The solution in fixed alkali carbonates deposits antimonious oxide on cooling and standing (*c*):

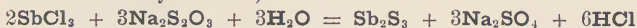


500. Hydrosulphuric acid precipitates, from not too strongly acidulated solutions of antimonious salts, the orange-red *antimonious sulphide*,  $\text{Sb}_2\text{S}_3$  (hydrated), slightly soluble in pure water, insoluble in water containing  $\text{H}_2\text{S}$ . In neutral solutions (tartrate) the precipitation is imperfect, non-acidulated solution of the potassio tartrate being only colored; in strong hydrochloric acid solutions and in strong alkaline solutions, the precipitation is prevented. Alkali sulphides give the same precipitate, soluble in excess of the reagents (*a*), then reproduced by acids as antimonious sulphide (*b*). The *antimonious sulphide is soluble* in fixed alkalies (*c*); in alkali sulphides, more readily if they contain excess of sulphur (*a*), and quite difficultly in normal (colorless) ammonium sulphide; only slightly soluble in ammonium hydroxide, and scarcely at all soluble in ammonium carbonate (distinction from arsenic, 459); slowly soluble by boiling solution of fixed alkali carbonate (*d*) (distinction from tin); soluble in hydrochloric acid, either moderately dilute or stronger (separation from arsenic, 459) (*e*); soluble in nitro-hydrochloric acid (*f*); insoluble in solutions of acid sulphites; left insoluble by nitric acid.

In the solutions in alkali sulphides, the antimonious sulphide exists as alkali thio salt; thioantimonate when from action of yellow ammonium sulphide (equation *a*):



**501. Thiosulphates**—as  $\text{Na}_2\text{S}_2\text{O}_3$ —likewise precipitate *antimonious sulphide* (separation of arsenic and antimony from tin):



**502. Potassium cyanide** gives a white precipitate.—**Ferrocyanides** (in absence of tartaric acid) give a white precipitate, insoluble in acids.—**Oxalic acid** (in absence of tartaric acid) gives a white crystalline precipitate, forming slowly but completely. **Potassium iodide** with hydrochloric acid in antimonious solutions gives only a yellow color—no free iodine (*distinction from antimonie acid*).

**503.** Antimonious oxide is **reduced to the elemental state** by agents, and with reactions, similar to those effecting the reduction of arsenious oxide.

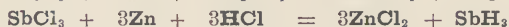
**Stannous chloride**, however, does not reduce it (*distinction from arsenic*).

The **metals**: magnesium, zinc, iron, cadmium, lead, tin, copper, and bismuth, precipitate from antimonious solutions (in absence of nitric acid) the brown-black *metallic antimony*:

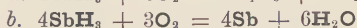
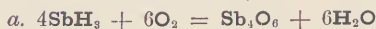


If antimony be reduced from a dilute hydrochloric acid solution by **zinc**, on **platinum** foil or in a platinum dish, the larger portion of the antimony is deposited as a brown or black *adherent coating* or stain on the platinum, while a portion passes off as antimonious hydride along with free hydrogen. The stain is removed by warm nitric, not by hydrochloric acid. In this test, tin deposits as a loose, spongy mass, soluble in hydrochloric acid, and arsenic does not closely adhere to the platinum (470).

**504.** If **hydrogen** be generated, more abundantly than in the operation last mentioned, by zinc with dilute sulphuric or hydrochloric acid, in a Marsh's apparatus, a smaller portion of antimony is deposited with the zinc, while *antimonious hydride*,  $\text{SbH}_3$ , is obtained for examination (compare arsenic. 463):



**505.** *Antimonious hydride* **burns** with a luminous and faintly bluish-green flame, dissipating vapors of antimonious oxide and of water (*a*); or depositing antimony on **cold porcelain** held in the flame, as a lustreless brownish-black *spot* (*b*). The gas is also decomposed by passing through a small glass tube heated to low redness, forming a lustrous ring or *mirror* in the tube. The spots and mirror of antimony are compared with those of arsenic in 466.



**506.** When the *antimonious hydride* is passed into a solution of **silver nitrate**, the silver is reduced, leaving all the antimony with the silver, as antimonious argentide,  $\text{Ag}_3\text{Sb}$ , a black precipitate (*distinction from arsenic*, which enters into solution, 467):



If the precipitate be removed and washed free from undecomposed silver salt (and arsenious acid, if that be present), the antimony may be dissolved out by boiling for some time with concentrated solution of tartaric acid (494 g). Also, **hydrochloric acid** readily dissolves the antimony from  $\text{Ag}_3\text{Sb}$ , though it cannot dissolve uncombined antimony. The solution

consists of antimonious chloride, leaving  $\text{AgCl}$ . The solution may be tested for antimony by hydrosulphuric acid. Also,  $\text{SbH}_3$  received in nitric acid changes to  $\text{Sb}_2\text{O}_3$ , insoluble in water (separation from As).

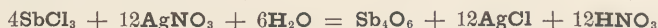
507. All compounds of antimony are completely reduced in the dry way on charcoal with sodium carbonate, more rapidly with potassium cyanide; the metal fusing to a brittle globule (compare 494). The reduced metal rapidly oxidizes, the white oxide rising in fumes, and making a crystalline deposit on the support. The same white oxide is formed on heating antimony or its sulphides in a glass tube, through which air is allowed to pass. The equations for reduction correspond to those given for arsenic in 471.

508. The oxidation of antimonious compounds to antimonic compounds requires strong oxidizing agents; that is, antimonious oxide is not a powerful reducing agent. The action of nitric acid and chlorine has been stated in connection with metallic antimony (494 *d* and *e*). Silver oxide (509), gold chloride (510), chromic acid (511), and permanganates, oxidize antimonious compounds, their reactions (especially the first-named) giving us delicate tests in distinction from antimonic compounds. For distinction of antimonic compounds, see, also, the oxidizing action of antimonic acid on iodides in 518.

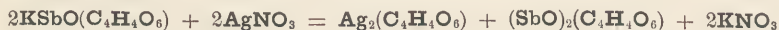
509. Solution of silver nitrate—with the potassium or sodium hydroxide solution of antimonious oxide,  $\text{KSbO}_2$ —gives a black precipitate of argentous oxide, of metallic silver (see equation), insoluble in ammonium hydroxide, and mixed with gray argentic oxide, which is dissolved out by the ammonia. If chlorides are present in the solution, the silver chloride produced will also dissolve in ammonium hydroxide, leaving only the black metallic silver. Now, the alkaline antimonates, formed if antimonic compound was present in the substance taken in this test, precipitate white silver antimonate, soluble in ammonium hydroxide (leaving still the evidence of antimonious compounds):



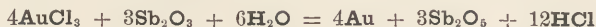
Silver nitrate, in acid solution of antimonious chloride, precipitates  $\text{Sb}_2\text{O}_3$  with  $\text{AgCl}$ , the latter dissolving in ammonium hydroxide, and leaving the former (no oxidation of the antimony being effected):



In solution of potassium antimonious tartrate, silver nitrate precipitates only silver tartrate, soluble in ammonium hydroxide, the antimonious oxide being held in solution as a tartrate. Thus:



510. Solution of auric chloride,  $\text{AuCl}_3$ , is reduced, in boiling (acid) solution of antimonious chloride, to metallic gold, as a yellow precipitate, mixed with antimonic oxide as a larger bulk of white precipitate, unless much excess of hydrochloric acid is present to hold antimonic chloride in solution (515):



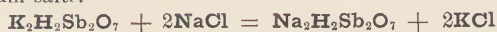
511. Chromic acid—obtained with  $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{HCl}$ —is reduced to chromic salt,  $\text{Cr}_2\text{Cl}_6$ , by acid antimonious solutions; the liquid turning green, and antimonic oxide,  $\text{Sb}_2\text{O}_5$ , being precipitated or left in solution—as a sparing or abundant excess of acid is present (515).

**512. Reactions of ANTIMONIC Salts.**—Antimonic oxide, or *anhydride*, is a yellowish powder, but slightly soluble in water; soluble in concentrated hydrochloric acid and in tartaric acid, scarcely at all in nitric acid. Antimonic chloride,  $\text{SbCl}_3$ , is completely decomposed by water; the sulphide,  $\text{Sb}_2\text{S}_3$ , insoluble in water.

There are two hydrogen antimonates or acids: *antimonic acid*,  $\text{H}_2\text{OSb}_2\text{O}_5$  or  $\text{HSbO}_3$ , monobasic; and *metantimonic acid*  $(\text{H}_2\text{O})_2\text{Sb}_2\text{O}_5$  or  $\text{H}_4\text{Sb}_2\text{O}_7$ , tetrabasic; the former being produced when antimony is dissolved by excess of nitric acid (494 d), or when an antimonate is decomposed by a stronger acid (515); the latter being formed in the decomposition of antimonic chloride by water. Free metantimonic acid holds  $2\text{H}_2\text{O}$  in addition to the basic water.

**513.** *Antimonic acid*,  $\text{HSbO}_3$ , is sparingly soluble in water, reddens litmus, and dissolves in concentrated hydrochloric acid, or, slowly, in a large proportion of water acidulated with that acid; also in tartaric acid. It dissolves, by combination, with cold solution of potassium hydroxide, but not in cold solution of ammonium hydroxide. By fusion with potassium hydroxide it is changed to a salt of metantimonic acid,  $\text{K}_4\text{Sb}_2\text{O}_7$ .—*Metantimonic acid*,  $\text{H}_4\text{Sb}_2\text{O}_7$  or  $(\text{H}_2\text{O})_2\text{Sb}_2\text{O}_5$ , is more soluble in water, in acids, and in ammonium hydroxide, than antimonic acid, into which it easily changes.

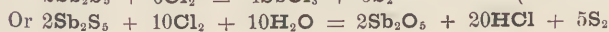
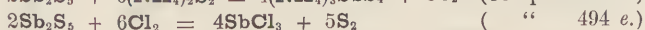
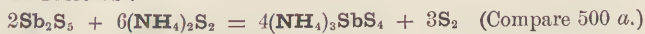
**514.** Metantimonic acid forms two classes of salts—normal, as  $\text{M}_4\text{Sb}_2\text{O}_7$ , and acid salts, as  $\text{M}_2\text{H}_2\text{Sb}_2\text{O}_7$ . Normal potassium metantimonate,  $\text{K}_4\text{Sb}_2\text{O}_7$ , is made by fusing one part of  $\text{KSbO}_3$  with about three parts of  $\text{KOH}$ . By treating this salt with water the acid salt, dipotassium dihydrogen metantimonate,  $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ , is formed. This salt is used to precipitate sodium salts.



It is prepared by fusing antimonic acid with large excess of potassium hydroxide; then dissolving, filtering, evaporating, and digesting hot, in syrupy solution, with large excess of potassium hydrate, best in a silver dish, decanting the alkaline liquor, and stirring the residue to granulate, dry. This reagent must be kept dry, and dissolved when required for use; inasmuch as, in solution, it changes to the tetrapotassium metantimonate, which does not precipitate sodium. The reagent is, of course, not applicable in acid solutions.

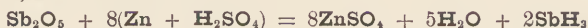
**515.** Slight additions of water precipitate the concentrated hydrochloric acid solutions of antimonic acid, or antimonic chloride, as tetra *metantimonic acid*,  $(\text{H}_2\text{O})_2\text{Sb}_2\text{O}_5$  or  $\text{H}_4\text{Sb}_2\text{O}_7$  (512); the precipitate being sparingly soluble in the acidulated liquid.—Acids precipitate, from solutions of alkali antimonates and metantimonates, the corresponding antimonic acid,  $\text{HSbO}_3$  or  $\text{H}_4\text{Sb}_2\text{O}_7$ . Tartaric acid prevents these precipitations.

**516.** Hydrosulphuric acid and sulphides precipitate the orange-colored *antimonic sulphide*,  $\text{Sb}_2\text{S}_3$ , having the solubilities stated for antimonic sulphide in 500—antimonic compounds forming in the solution. Both tetrabasic and tribasic sulphantimonates are formed. The typical, tribasic salts occur as follows:





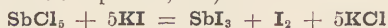
517. Antimonic acid is reduced to metal by all the reducing agents stated for antimonious oxide in 503, having the same behavior with zinc and platinum, and in Marsh's test :



Stannous chloride reduces antimonie to antimonious compounds, but, as stated in 503, does not reduce the latter :



518. Antimonic acid is reduced to *antimonious iodide* by hydriodic acid, as follows (distinction from antimonious compounds, 502) :



If **potassium iodide** is added to hydrochloric acid solution of antimonie compounds, a dark brown precipitate of iodine appears ; if only antimonious compound is present, the solution is colored yellow, but remains clear. In both cases, free hydriodic acid is formed. If the proportion of antimonie compound be very slight, the liberated iodine will still be revealed by its violet color in the subsiding layer, after agitation with carbon disulphide and subsidence. Of course, the liquid and the hydrochloric acid must be strictly free from uncombined chlorine, and the iodide must contain no iodate—that is, the two reagents must not precipitate each other.

519. By **ignition**, in the absence of reducing agents, antimonie acid and anhydride are reduced to antimonious antimonate,  $\text{Sb}_2\text{O}_3\text{Sb}_2\text{O}_5$ , or  $\text{Sb}_2\text{O}_4$  ; a compound unchanged at a red heat, and obtained for quantitative determinations.

520. The antimonates of the fixed alkali metals are not vaporized or decomposed when **ignited** in absence of reducing agents. Hence, by **fusion** in the crucible with soda and oxidizing agents—i.e., with **sodium nitrate** and **carbonate**—the compounds of antimony, and of arsenic (486), are converted into non-volatile sodium metantimonate and arsenate,  $\text{Na}_4\text{Sb}_2\text{O}_7$  and  $\text{Na}_3\text{AsO}_4$ . If now the fused mass be digested and disintegrated in cold water and filtered, *the antimonate is separated as a residue* ( $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ —513), *while the arsenate remains in solution* with the excess of alkali. The operation is much more satisfactory when the arsenic and antimony are previously fully oxidized—as by digestion with nitric acid—as the oxidation by fusion in the crucible is not effected soon enough to retain all of the arsenic or antimony which may be in the state of lower oxides, sulphides, etc. If compounds of **tin** are present in this operation—and if the fusion is not done with excess of heat, so as to convert sodium nitrite to caustic soda and form the soluble sodium stannate—the tin will be left as stannic oxide,  $\text{SnO}_2$ , in the residue with the  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ . But if sodium hydroxide is added in the operation, the tin is separated as stannate in solution with the arsenic. A plan of separations is based on these facts.

521. **Estimation.**—(1) Tartaric acid and water are added to  $\text{SbCl}_3$ , which is then precipitated by  $\text{H}_2\text{S}$  as  $\text{Sb}_2\text{S}_3$ , and after washing on a weighed filter it is dried at  $100^\circ \text{C}$ . and weighed. If from any cause the precipitate contains free sulphur it is separated by heating in  $\text{CO}_2$ . (2) Antimonious oxide, sulphide, or any oxy salt of antimony is first boiled with fuming ni-



tric acid, which converts it into  $\text{Sb}_2\text{O}_3$ , and then by ignition it is reduced to  $\text{Sb}_2\text{O}_4$ , and weighed as such. (3) The trichloride is precipitated by gallic acid, and weighed after drying at  $100^\circ \text{C}$ . (4) Volumetrically.  $\text{Sb}'''$  is oxidized to  $\text{Sb}^v$  in presence of  $\text{NaHCO}_3$  by a titrated solution of iodine. The end of the reaction is shown by the blue color given to starch. (5) Volumetrically.  $\text{Sb}'''$  is oxidized to  $\text{Sb}^v$  in presence of  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  by  $\text{K}_2\text{Mn}_2\text{O}_8$ . (6) Volumetrically.  $\text{Sb}'''$  is oxidized to  $\text{Sb}^v$  by  $\text{K}_2\text{Cr}_2\text{O}_7$ , and the excess of  $\text{K}_2\text{Cr}_2\text{O}_7$  used is determined by a graduated solution of  $\text{FeSO}_4$ ,  $\text{K}_6\text{Fe}_2(\text{CN})_{12}$  being used to show the end of the reaction.

**522. Oxidation.**— $\text{Sb}''' \text{H}_3$  is decomposed by heat alone into  $\text{Sb}^\circ$  and  $\text{H}$  (505). By burning in a limited supply of air it is oxidized to  $\text{Sb}^\circ$ ; and with free access of air to  $\text{Sb}'''$ ,  $\text{Sb}_4\text{O}_6$  being formed. Passed into a solution of  $\text{SbCl}_3$  or of  $\text{KOH}$ , sp. gr. 1.25,  $\text{Sb}^\circ$  is produced. Passed into  $\text{AgNO}_3$ ,  $\text{SbAg}_3$  is precipitated. With excess of  $\text{Cl}$ ,  $\text{Br}$ , or  $\text{HNO}_3$  in presence of water  $\text{Sb}^v$  is formed; and with excess of  $\text{SbH}_3$  metallic  $\text{Sb}^\circ$  is precipitated. Excess of iodine with water forms  $\text{Sb}'''$ ; but with excess of  $\text{SbH}_3$  metallic  $\text{Sb}^\circ$  is produced.  $\text{SbH}_3$  is also oxidized by  $\text{HgCl}_2$ ,  $\text{K}_2\text{Mn}_2\text{O}_8$ , etc.

$\text{Sb}'''$  is oxidized to  $\text{Sb}^v$  by  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{HClO}_3$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{CrO}_4$ ,  $\text{K}_2\text{Mn}_2\text{O}_8$ , etc.  $\text{Sb}^v$  is reduced to  $\text{Sb}'''$  by  $\text{HI}$  and  $\text{SnCl}_2$ ; and both  $\text{Sb}^v$  and  $\text{Sb}'''$  are reduced to metallic  $\text{Sb}^\circ$  by  $\text{Zn}$ , but in presence of a dilute acid, such as  $\text{H}_2\text{SO}_4$ ,  $\text{Sb}''' \text{H}_3$  is evolved.

**TIN.**  $\text{Sn} = 117.698$ .

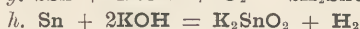
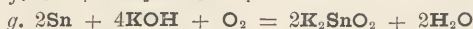
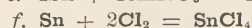
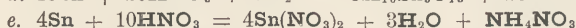
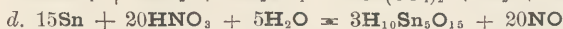
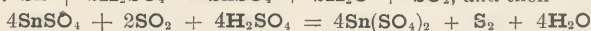
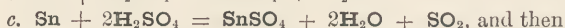
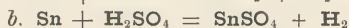
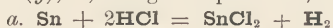
**523.**—*Specific gravity*, 7.294 (MATTHIESSEN, 1866). *Melting point*,  $232.7^\circ \text{C}$ . ( $451^\circ \text{F}$ .) (PERSON, 1847). Boils between  $1450^\circ$  and  $1600^\circ \text{C}$ . (CARNELLEY and WILLIAMS, 1879). Valence, a dyad in  $\text{Sn}''\text{Cl}_2$  and in all stannous compounds; a tetrad in  $\text{Sn}^{\text{iv}}\text{Cl}_4$ , and in all stannic compounds.

**524. Occurrence.**—Rarely found native. Its chief ore is cassiterite, or tin stone, a more or less pure dioxide,  $\text{SnO}_2$ . Less frequently found in tin pyrites,  $\text{Cu}_4\text{SnS}_4 + (\text{FeZn})_2\text{SnS}_4$ . Occasionally found as a silicate, and in small quantities in various minerals.

**525. Preparation.**—The reducing agent employed is carbon. The impure ore,  $\text{SnO}_2$ , is first roasted, which removes some of the arsenic as  $\text{As}_4\text{O}_6$ , and some of the sulphur as  $\text{SO}_2$ . Then, by washing, the soluble and some of the insoluble impurities are washed away, the heavier  $\text{SnO}_2$  remaining. It is then fused with powdered coal, lime being introduced to form a fusible slag with the earthy impurities. It is refined by repeated fusion. Strictly pure tin is best made by treating the refined tin with  $\text{HNO}_3$ , and then reducing the oxide thus formed by fusion with charcoal; or by reducing the purified chloride.

**526. Properties.**—A lustrous white metal, fusible at  $232.7^\circ \text{C}$ . ( $451^\circ \text{F}$ .), volatile (when not in contact with the air) at a white heat.—It tarnishes a very little in pure air or

with moisture, but more in air containing hydrosulphuric acid ; at a white heat it burns in the air with a dazzling white light, and formation of stannic oxide; at a red heat it decomposes steam with evolution of hydrogen.—It **dissolves** with hydrochloric acid, slowly when the acid is dilute and cold, but rapidly when hot and concentrated—stannous chloride and hydrogen being produced (*a*); in dilute sulphuric acid, slowly, with separation of hydrogen (*b*); in hot concentrated sulphuric acid, rapidly, with separation of sulphurous anhydride and sulphur (*c*); nitric acid rapidly converts it into metastannic acid, insoluble in acids (*d*); very dilute nitric acid dissolves it without evolution of gas as stannous nitrate and ammonium nitrate (*e*); nitro-hydrochloric acid dissolves tin easily as stannic chloride (*f*), potassium hydroxide solution dissolves it very slowly, and by atmospheric oxidation (*g*); or, at high temperatures, with evolution of hydrogen (*h*).

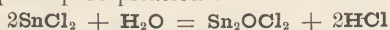


**527.** Tin forms two stable oxides and corresponding **classes of salts**: stannous oxide,  $\text{Sn}''\text{O}$ , and stannic oxide,  $\text{Sn}'''\text{O}_2$ ; the latter acts both as a base, in stannic compounds, and as an acidulous anhydride, in stannates of metals. Stannous compounds readily change to stannic compounds by contact with the air and by nearly all oxidizing agents (537), being themselves powerful reducing agents; stannic compounds are not easily reduced to stannous combinations, being feeble oxidizing agents. In respect to the relative stability of its two classes of salts, tin resembles iron; stannous salts, however, are relatively less permanent than ferrous salts—in accordance with the fact that stannic sulphide is formed, and ferric sulphide is not formed, in precipitation by sulphides.

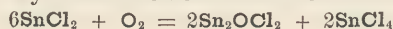
**528. STANNOUS** oxide, hydroxide, sulphide, oxychloride, phosphate, and oxalate are **insoluble** in water. The chloride requires quite strongly, and the nitrate moderately, acidulated water for solution; the bromide, the iodide, and sulphate dissolve in pure water (326).

Tin is **separated**, as a sulphide, with arsenic and antimony, from other second-group sulphides, by solution with yellow ammonium sulphide (555); from arsenic and antimony it is easily separated by reduction in Marsh's test (535). Stannous salts are distinguished by their reducing power (537).

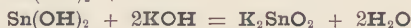
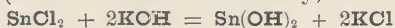
**529. Water** partially decomposes the acidulated solution of stannous chloride; precipitating *stannous oxychloride*, soluble in acids, the liberated acid preventing complete precipitation:



The **atmosphere** causes, in solutions of stannous chloride, a precipitate of *stannous oxychloride* with formation of *stannic* chloride; a change which occurs in the reagent kept in bottles frequently opened, and is retarded by presence of sufficient hydrochloric acid with metallic tin.



**530.** The **alkali hydroxides** precipitate, from solutions of stannous salts, *stannous hydroxide*,  $\text{Sn}(\text{OH})_2$ , white, readily soluble in excess of the fixed alkali hydroxides, as alkali stannite,  $\text{K}_2\text{SnO}_2$ , insoluble in ammonium hydroxide (distinction from antimony):



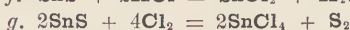
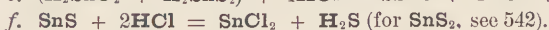
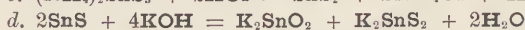
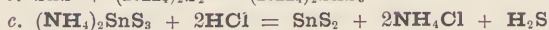
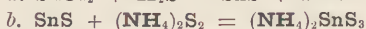
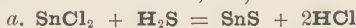
By boiling, the precipitate becomes anhydrous,  $\text{SnO}$ , without change of color. Boiling in strong potassium hydroxide solution, more quickly by the addition of a little tartaric acid, blackens the precipitate, which now contains metallic tin.



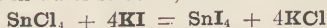
**Alkali carbonates** also precipitate *stannous hydrate*, insoluble in excess (distinction from antimony). Barium carbonate precipitates all the tin as hydroxide, in the cold.

**531. Hydrosulphuric acid** and sulphides precipitate the dark-brown *stannous sulphide*,  $\text{SnS}$  (*a*), hydrated, insoluble in dilute, soluble in moderately dilute acids, as stated below. Thiosulphates do not give a precipitate—distinction from arsenic (459), and from antimony (501).

*Stannous sulphide* is readily dissolved by alkali supersulphides, the yellow sulphides, with formation of thiostannates (*b*), from which acids precipitate the yellow *stannic sulphide* (542) (*c*), but the normal, colorless, alkali sulphides scarcely dissolve any stannous sulphide. **Potassium and sodium hydroxides** dissolve it as *stannites* with thiostannites (*d*), from which acids precipitate again the brown *stannous sulphide* (*e*); ammonium hydroxide and the alkali carbonates do not dissolve it (distinction from arsenic, 459, and with fixed carbonates distinction from antimony, 500 *d*). It is not soluble by acid sulphites (distinction from arsenic, 459).—**Hydrochloric acid** dissolves it, as *stannous chloride*, with evolution of hydrosulphuric acid (*f*); nitro-hydrochloric acid—free **chlorine**—as *stannic chloride* with residual sulphur (*g*); nitric acid oxidizes it to metastannic acid, without solution (separation from arsenic, 560).



**532. Potassium iodide** precipitates—from solutions not very dilute, as nearly neutral as possible and free from stannic salt—the yellow *stannous iodide*,  $\text{SnI}_2$ , sparingly soluble in water, more soluble in warm than cold water, and slightly decomposed by water with precipitation of variable, yellow, stannous oxy-iodides; slightly soluble in excess of the reagent, the potassium stannous iodide being mostly decomposed by water, less in dilute solutions; soluble in hydrochloric acid, and in solution of potassium hydroxide. With **stannic salts** in water solution, the iodides react as follows (see 539):



And, simultaneously:  $\text{SnI}_4 + 3\text{H}_2\text{O} = \text{SnO}(\text{OH})_2 + 4\text{HI}$

**533. Alkaline phosphates** precipitate *stannous phosphate*,  $\text{Sn}_2(\text{PO}_4)_2$ , white, variable by conditions.—**Oxalates** precipitate *stannous oxalate*,  $\text{SnC}_2\text{O}_4$ , white.—**Ferrocyanides**

give a white gelatinous precipitate; **ferricyanides**, a white precipitate (with stannic salts, no precipitate).—**Cyanides** precipitate *stannous hydroxide*, with liberation of hydrocyanic acid.

**534.** Tin is **reduced by zinc**: from freely acidulated stannous or stannic solutions, as a gray *spongy mass* (**Sn**); from alkaline solutions, as lustrous crystals. With **zinc on platinum** foil or in a platinum dish, the tin reduced, from acid solutions, collects mostly on the zinc, does not stain or adhere to the platinum, and, however reduced, *dissolves in hydrochloric acid* (526 a) (distinctions from antimony and from arsenic; see 503). But reduction by metallic **aluminium**, or **magnesium**, is much more prompt and satisfactory.

**535.** In Marsh's Test for arsenic (463) and antimony (504), if tin is present, it will be deposited as a dark-colored powder, as stated in the preceding paragraph, not adherent to the zinc. Arsenic is deposited early in the operation, and finally all removed in the gas; antimony is not wholly but is mostly removed, at the last; tin, not at all. If all the zinc is permitted to dissolve while the acid is not expended, the deposit of tin will slowly dissolve in the dilute acid. Indeed, tin may be used instead of zinc, in Marsh's Test. With zinc present, the tin does not dissolve; and after the arsenic has all been expelled in the gas, *the tin may be rinsed away from the zinc by the water-jet, and dissolved with moderately concentrated hydrochloric acid*, while any antimony present remains undissolved (526 a, and 494 a). The antimony may afterwards be quickly dissolved by nitrohydrochloric acid, and tested.

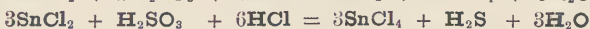
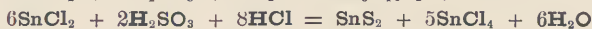
**536.** Before the **blow-pipe**, on **charcoal**, with sodium carbonate, and more readily by addition of potassium cyanide, tin is reduced to malleable lustrous globules—brought to view (if minute, under a magnifier) by repeated trituration of the mass with water, and decantation of the lighter particles. A little of the white incrustation of stannic oxide will collect on the charcoal near the mass, and, by persistence of the flame on the globules, the same coating forms upon them. This coating, or oxide of tin, moistened with solution of **cobalt nitrate**, and again ignited strongly, becomes of a blue-green color.

**537.** Stannous salts are **oxidized to Stannic Salts** by a large number of reagents (see 527). Stannous chloride is one of the most convenient and efficient of the ordinary, discriminative deoxidizing agents for operations in the wet way. As stannic chloride is soluble in the solvents of stannous chloride, no precipitate of tin is made by its reducing action; but many other metals are so precipitated by reduction to insoluble forms. Thus

**Mercuric** chloride is reduced from solution, first to white *mercurous* chloride, and then to gray *mercury* (448 a); **silver** nitrate, to brown-black silver (420): **arsenic**, from arsenic to arsenious compounds (468 e), and all soluble compounds to black precipitate of *arsenic*;



**antimonic** compounds, to soluble antimonious compounds (517); bismuth salts, to monoxide (366); **chromic acid**, to green *chromic* salt, left in solution; **ferric** salts, to *ferrous* salts, left in solution; **auric** chloride, to the violet precipitate of *gold*. **Sulphurous anhydride**, in ordinary relations a strong reducing agent, serves to oxidize stannous chloride; warm digestion with sulphites and hydrochloric acid giving a precipitate of  $\text{Sn}_6\text{O}_{10}\text{S}_2$  or  $\text{SnS}_2$ , or evolving  $\text{H}_2\text{S}$ , depending upon the amount of free **HCl** present.



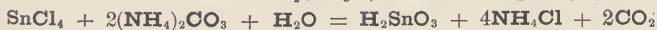
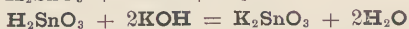
Nitric acid changes stannous to stannic compounds, chiefly with formation of *nitric oxide*.—**Ferricyanides** effect the same change, with formation of *ferrocyanides*; and **permanganates**, with production of *manganous salts*. Many of these reactions are applicable in **distinguishing stannous from stannic salts**. A very dilute mixture of ferricyanide and ferric salt makes a delicate though not distinctive test for tin as a dyad.

**538. STANNIC** oxide or anhydride forms two well-marked hydroxides or acids: *stannic acid*,  $\text{H}_2\text{SnO}_3$ , and *metastannic acid*,  $\text{H}_{10}\text{Sn}_5\text{O}_{15}$  (variable). Stannic acid is formed by precipitating stannic salts with alkalies (540); metastannic acid, by action of nitric acid on tin (526 d).

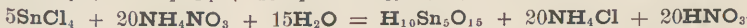
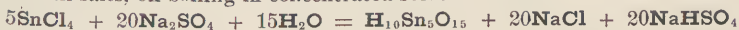
*Stannic acid* is **insoluble** in water, but readily forms soluble stannic salts with hydrochloric, sulphuric, and nitric acids, and soluble alkali stannates with the alkali hydroxides, other stannates being insoluble. *Metastannic acid* is insoluble in acids, and does not form metastannic salts; but dissolves in fixed alkalies, with formation of metastannates.

**539.** The *stannic* oxide, hydroxide, sulphide, and phosphate are **insoluble** in water. The chloride and bromide are scarcely at all decomposed by water; the iodide, wholly decomposed by water (see equation, 532). The relations of stannous chloride, bromide, and iodide, to water, are each quite the reverse of the corresponding stannic haloids, as shown by comparison with 528. Stannic sulphate is decomposed by boiling its water solution. Stannic chloride and iodide are soluble in alcohol.

**540.** The **alkali hydroxides** and **carbonates**, and barium carbonate, precipitate, from solutions of stannic salts, *stannic acid*,  $\text{H}_2\text{SnO}_3$ , white; soluble in excess of fixed alkali hydroxides and carbonates; insoluble in ammonium hydroxide and carbonate (distinction from antimony). The alkaline solutions contain stannates:

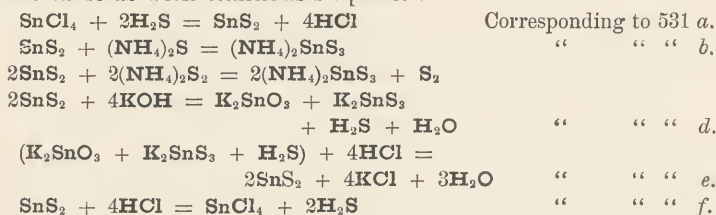


**541.** A peculiar precipitation of *metastannic acid*,  $\text{H}_{10}\text{Sn}_5\text{O}_{15}$ , is produced by most normal alkali salts, on boiling in concentrated solution. Thus:



**542.** **Hydrosulphuric acid** and sulphides precipitate *stannic sulphide*,  $\text{SnS}_2$ , hydrated, yellow, having the solubilities given in 531 for stannous sulphide, with this difference, that stannic sulphide is moderately soluble

in normal, colorless, alkali sulphides. With the stannic sulphide precipitate, yellow, we have these reactions, *different from those in 531*; the others being the same as with stannous sulphide :



**Phosphates** precipitate basic *stannic phosphate*,  $\text{Sn}_2\text{O}(\text{PO}_4)_2$ , white ; **Ferrocyanides** give a white, and **ferricyanides** no precipitate.

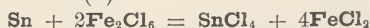
Stannic salts are **reduced to Stannous Salts** by metallic tin or copper.



Concerning the reduction of stannic compounds to metal, see 534, and **blow-pipe reactions**, 536.

The behavior of stannic oxide in fusion with sodium hydroxide and carbonate—used in separation from antimony and from arsenic—is described in 525.

**543. Estimation.**—(1) Gravimetrically. It is converted into  $\text{SnO}_2$ , and after intense ignition weighed. (2) Volumetrically. To  $\text{SnCl}_4$  add  $\text{KNaC}_4\text{H}_4\text{O}_6$  and  $\text{NaHCO}_3$ , then some starch solution and a graduated solution of iodine, until a permanent blue coloration appears. (3) To  $\text{SnCl}_4$  add slight excess of  $\text{Fe}_2\text{Cl}_6$ , and determine the amount of  $\text{FeCl}_2$  formed, by a graduated solution of  $\text{K}_2\text{Mn}_2\text{O}_8$ . (4) Reduce to metallic tin, then dissolve in  $\text{Fe}_2\text{Cl}_6$ , and proceed as in (3).



**544. Oxidation.**—Solutions of  $\text{Sn}^{\text{IV}}$  and  $\text{Sn}^{\text{II}}$  are reduced to metallic tin by Zn, Cd, Al, and Mg. Metallic tin reduces solutions of Bi, Cu, Hg, Ag, Pt, and Au to the metallic state.  $\text{Sn}^{\text{II}}$  is oxidized to  $\text{Sn}^{\text{IV}}$  by free  $\text{HNO}_2$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$  (if hot),  $\text{HClO}_3$ , Cl,  $\text{HClO}$ , Br,  $\text{HBrO}_3$ , I,  $\text{HIO}_3$ ,  $\text{H}_6\text{Fe}_2(\text{CN})_{12}$ . Also by  $\text{Pb}^{\text{IV}}$ ,  $\text{Ag}^{\text{I}}$ ,  $(\text{Hg}_2)^{\text{II}}$ ,  $\text{Hg}^{\text{II}}$ ,  $\text{As}^{\text{V}}$ , ( $\text{As}^{\text{III}}$  in presence of  $\text{HCl}$ ),  $\text{Sb}^{\text{V}}$ ,  $\text{Cu}^{\text{II}}$ ,  $(\text{Fe}_2)^{\text{VI}}$ ,  $\text{Fe}^{\text{VI}}$ ,  $\text{Cr}^{\text{VI}}$ ,  $(\text{Co}_2)^{\text{VI}}$ ,  $(\text{Ni}_2)^{\text{VI}}$ ,  $(\text{Mn}_2)^{\text{VI}}$ ,  $\text{Mn}^{\text{IV}}$ ,  $\text{Mn}^{\text{VI}}$ , and  $\text{Mn}^{\text{VII}}$ . As a rule, non-metallic acids must be free, or no action takes place. That is, in alkaline mixture they do not oxidize  $\text{Sn}^{\text{II}}$  at ordinary temperatures. But metallic acids and the above-mentioned metallic forms oxidize  $\text{Sn}^{\text{II}}$ , both in acid and alkaline mixtures. Free Cl, Br, and I act even more rapidly in alkaline than in acid mixtures.

## 545. Comparison of Certain Reactions of Arsenic, Antimony, and Tin.

*Taken as Arsenious Oxide, Antimonious Chloride, Stannous Chloride, or other soluble Compounds.*

	As'''	Sb'''	Sn''
<b>H<sub>2</sub>S</b> forms colored sulphides, soluble in $(\text{NH}_4)_2\text{S}_2$ , and in alkalies, reprecipitated by acids.	<b>As<sub>2</sub>S<sub>3</sub></b> , yellow, insoluble in <b>HCl</b> , soluble in $(\text{NH}_4)_2\text{CO}_3$ (459).	<b>Sb<sub>2</sub>S<sub>3</sub></b> , orange, soluble in <b>HCl</b> , insoluble in $(\text{NH}_4)_2\text{CO}_3$ (500).	<b>SnS</b> ; brown ( <b>SnS<sub>2</sub></b> yellow), soluble in <b>HCl</b> , insoluble in $(\text{NH}_4)_2\text{CO}_3$ (531).
<b>NH<sub>4</sub>OH</b> in excess.	No precipitate.	<b>Sb<sub>2</sub>O<sub>3</sub></b> , white (498).	<b>Sn(OH)<sub>2</sub></b> , white (530).
<b>Zn</b> and dilute <b>H<sub>2</sub>SO<sub>4</sub></b>	<b>AsH<sub>3</sub></b> (gas) (463). In <b>AgNO<sub>3</sub></b> , forms <b>Ag</b> and <b>H<sub>3</sub>AsO<sub>3</sub></b> (467).	<b>SbH<sub>3</sub></b> (gas) (504). In <b>AgNO<sub>3</sub></b> forms <b>Ag<sub>3</sub>Sb</b> , black precip. (506).	<b>Sn</b> , a gray mass (535).
<b>Dilution</b> of saturated solutions.	.....	<b>SbOCl</b> , white. Dissolved by tartrate (497).	<b>Sn<sub>2</sub>OCl<sub>2</sub></b> , white (529).
<b>HNO<sub>3</sub></b> , concentrated, acting on the solids.	<b>H<sub>3</sub>AsO<sub>4</sub></b> (475). Gives certain of the reactions of <b>H<sub>3</sub>PO<sub>4</sub></b> (478).	<b>Sb<sub>2</sub>O<sub>4</sub></b> and <b>Sb<sub>2</sub>O<sub>5</sub></b> , insoluble (494 d and 508).	<b>H<sub>10</sub>Sn<sub>2</sub>O<sub>15</sub></b> , insoluble (526 d, and 537).

## SEPARATION OF THE METALS OF THE FIRST AND SECOND GROUPS.

546. The separation of the **First-Group metals**—lead, silver, and mercury of mercurous salts—from the bases of the **Second-Group**, by *hydrochloric acid*, is complete for silver and mercury, but incomplete for lead (390). Lead could be separated from other second-group metals by *sulphuric acid* in *dilute* solution; but this applied to the original solution would also precipitate the fourth-group metals, and requires a different grouping of the bases, as by Zettnow's process (572). So it is identified, if abundant, in the first group, and then removed in the second group (after the separation by ammonium sulphide) by *sulphuric acid*. In removing lead as a sulphide, if hydrochloric acid is present, the solution should be quite dilute (390).

547. Although the only insoluble metallic chlorides are the plumbic, argentic, and mercurous, yet *hydrochloric acid* may produce precipitates in certain solutions which contain no first group base. The following are some of the conditions in which this occurs:

a. An acid solution of antimony, bismuth, or tin, with some other acid than hydrochloric, and saturated with water, as far as possible without precipitation, on the addition of hydrochloric acid, precipitates the *oxychloride* of the metal in question. These precipitates are readily soluble in excess of the hydrochloric acid, but so is a very slight precipitate of silver chloride (409).

b. In a saturated solution of certain salts, as barium chloride, hydrochloric acid precipitates the salt *without chemical change*; the precipitate soluble in a small proportion of water.

c. In solutions of higher sulphides, as  $\text{Na}_2\text{S}_2$  (459 c), and of thiosulphates, as  $\text{Na}_2\text{S}_2\text{O}_3$ —these solutions having an alkaline reaction—hydrochloric acid forms a precipitate of *sulphur*.

d. The solutions containing *double sulphides* of alkali metals and arsenic, antimony, tin (gold, platinum, molybdenum, iridium); *double iodides* of bismuth, copper, and first-group metals; *double cyanides* of class (1) (see Part II.), and certain *double thiosulphates*, are liable to precipitation in the first group. All these precipitates, except free sulphur,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_5$ , and those of first-group metals, are soluble in excess of the hydrochloric acid.

e. All the alkaline solutions of metallic oxides, as potassium zincate, are precipitated at the neutral point in the addition of acids.

f. Alkaline solutions of antimonic, silicic, boracic (tungstic, molybdic, tantallic, and niobic) acids; also of benzoic, salicylic, uric, and certain other organic acids, are precipitated by acidulation with mineral acids, many of the precipitates being soluble in hydrochloric acid. (Thallous salts are precipitated as chloride.)

g. Acidulation with hydrochloric acid may induce changes of oxidation or reduction, which, in certain mixtures, result in precipitation.

If the solution taken for the grouping of the bases has an alkaline reaction, it cannot contain a normal salt of a first-group base; it may contain a basic lead salt, or one of the compounds noticed in c, d, e, or f.

If the first-group precipitate be more than very slightly soluble by farther addition of water or of hydrochloric acid, it should be so dissolved before proceeding with the analysis. If the precipitate is colored, or if it is found not to accord with the reactions of any of the first-group bases, it should be treated separately, as a solid substance taken for examination.

**548.** The separation of the **First-Group bases from each other**, according to the **Table** given in Part III., is exceedingly simple.  $\text{PbCl}_2$  is dissolved in abundance of *hot water*;  $\text{AgCl}$ , in *ammonium hydroxide*; while  $\text{Hg}_2\text{Cl}_2$  is left insoluble in a characteristic black form, as  $\text{NH}_3\text{Hg}_2\text{Cl}$ .

If the lead chloride is not all washed out with hot water, the ammonium hydroxide will change it to insoluble basic salt (387), and leave it with the mercury on the filter.

Let it be observed, if the first-group precipitate contains but one base, the action of ammonium hydroxide determines which it is; lead chloride does not change color; silver chloride dissolves; mercurous chloride blackens.

**549.** The presence of **lead** is easily ascertained in the dilute solution of its chloride. A portion of this solution is treated for the sulphate, according to the **Table** given in Part III., carefully avoiding excess of acid (389);



an illustration of the important *relations of lead salts with sulphates*. Other portions of this dilute solution give the more delicate test with hydrosulphuric acid, and the characteristic test with chromates, and serve to illustrate the important relations with carbonates and phosphates; but a more concentrated solution must be used in studying the precipitates which are soluble in excess of their precipitants—those by fixed alkali hydroxides, iodides, bromides, etc. (Concerning lead in second-group relations, see 567.) Among the other tests made in study of first and second group metals, those involving reduction by metals and other agents should never be neglected.

**550.** The presence of **silver**, in its ammoniacal first-group solution, is determined according to the Table by reprecipitation with nitric acid, as **AgCl**. This test is exceedingly delicate, provided too much alkali chloride is not formed in the solution (409). For small quantities, it is better to expel the excess of ammonium hydroxide by heat before adding the nitric acid, which must not be in excess.

For farther illustrative tests, reduce the chloride to metallic silver, either by zinc, set aside in the test-tube, or by stannous salts, or sugar with alkali; then wash the reduced silver thoroughly, and dissolve it in nitric acid, as **AgNO<sub>3</sub>**.

**551.** The remaining base, **mercury**, as the black nitrogen dihydrogen dimercurous chloride, for the farther tests in the wet way, may be obtained as soluble mercuric salt by solution in nitro-hydrochloric acid. Good evidence of the mercurous combination of the mercury has been obtained in the first-group precipitation, and in the color of the product with ammonium hydroxide; but if the original solution is found not to contain other interfering metals, it may afterwards be used to obtain the distinctive reactions of mercurous salts with iodides, chromates, phosphates, etc.

**552.** In the **precipitation of the Second Group**, the *acidulation* requires attention. It must not be omitted because of an acid reaction of the original solution, unless it is known that free mineral acid is present. It must be sufficient for the formation of arsenious sulphide (459), and not too strong for complete precipitation of antimonious sulphide (500 e). If the original solution is strongly acid—as after solution of dry substances by mineral acids—the excess of acid must be reduced by evaporation. Free chlorine is incompatible with the group precipitant, and if present must be fully expelled.

**553.** Precipitates may occur in the second group, when no second-group metal is present. The precipitations by mere acidulation have been excluded by the first-group work, but the precipitation of free sulphur may occur, as follows: (a) with fading of a previous brownish-yellow tint, from ferric salts (214); (b) appearing with a green color, deeper than a previously existing red or yellow color, or from nearly colorless solutions, due

to chromic acid (194 *a*); (*c*) from free chlorine, bromine, or iodine, liberated by the dilute acid of the group reagents acting with chlorates, nitrates, bromates, iodates, hypochlorites, etc., of the original substance. Indeed, several of these substances decompose hydrosulphuric acid without the aid of other acids.

All the bases precipitated in the second group are thrown down as *colored* sulphides—yellow, orange, brown, or black—readily distinguishable from sulphur by the lighter color and the lighter specific gravity of the latter. The precipitate of sulphur may be disregarded—except as an indication of the possible presence of some of the oxidizing agents, and, with the changes of color mentioned in (*a*) and (*b*), especially indicative that iron or chromium will be found in the next group.

**554.** It will be remembered that **pentad arsenic** is not precipitated short of treatment with the hydrosulphuric acid gas for several hours (477). Unless this time can be taken, the arsenic must be reduced to arsenious acid—by sulphurous acid (484 *a*) or otherwise—or the systematic course of analysis may be departed from. In the latter case, the original solution may be used in Marsh's Test, if it do not contain nitrates or other oxidizing agents; or the reduction in the dry way (471) may be employed.

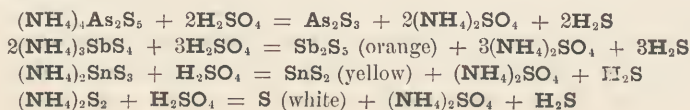
**555.** The **separation of the bases of the Second Group**, according to the **Table**, Part III., begins with a division into three classes, by action of two solvents, yellow ammonium sulphide and moderately concentrated nitric acid. We have, *in the precipitated sulphides* :

- (1) **As, Sb, Sn**—dissolved as thiosalts by  $(\text{NH}_4)_2\text{S}_2$ .
- (2) **Pb, Cu, Bi, Cd**—dissolved as nitrates by  $\text{HNO}_3$ .
- (3) **Hg**—dissolved as chloride by **Cl**.

**556.** Before applying **ammonium sulphide**, the precipitate of sulphides must be washed clean of acid, and of all substances in the filtrate. Whether the digestion is performed on the filter, or in the test-tube or beaker, the amount of solvent should be as small as possible.

The insoluble portion is filtered out, washed first with a little sulphide of ammonium, then with several portions of hot water, and set aside.

It is first to be determined whether any base has been dissolved by the sulphide of ammonium. This may be done, in a small portion, by a drop of dilute acid; if the precipitate be white, uncolored, either no sulphides of **As, Sb, Sn** were in the group precipitate, or they were in small proportion, and overwhelmed by the solvent. We place here together the representative equations :



It is evidently easy to mask the color of the sulphides by an excessive proportion of free sulphur, some of which will always be present; and, in case of any doubt, perhaps, as a general practice, it is better to proceed with the ammonium sulphide solution, to the final tests for arsenic, antimony, and tin.

**557.** There is this imperfection in the separation of **As**, **Sb**, and **Sn**, as sulphides, by ammonium sulphide: that **copper** as sulphide is slightly dissolved by the same solvent (342). Acids reprecipitate the copper sulphide, generally as normal **CuS**, but sometimes as a liver-colored super-sulphide, which, with excess of sulphur, has nearly the color of **SnS<sub>2</sub>**, or **As<sub>2</sub>S<sub>3</sub>**. The amount of copper so dissolved and reprecipitated is small, and cannot simulate notable quantities of arsenic, antimony, or tin; but such a small loss of copper from the nitric acid solution of the group lessens the delicacy of the work for that metal. Therefore, it is especially important to *identify copper in the preliminary examination*—by the bead or on charcoal if the substance is solid, and by the tint if in solution, and by the reduction on a strip of clean iron (346).

Now, the *fixed alkali super-sulphides*—**Na<sub>2</sub>S<sub>2</sub>** or **K<sub>2</sub>S<sub>2</sub>**—do not dissolve copper sulphide in the least, and they serve as solvents of the sulphides of **As**, **Sb**, and **Sn**, as well as ammonium sulphide; but they dissolve mercuric sulphide to an extent that involves a greater imperfection in the separations of the group than does the use of ammonium sulphide. However, if the preliminary examination shows mercury to be absent, it is better to use fixed alkali sulphide for the separation of copper from arsenic, antimony, and tin.

**558.** Having removed the bases soluble as ammonium thio-salts from the rest of the group, we have to separate **arsenic, antimony, and tin from each other**. This may be accomplished in several ways by certain solvents, acting on the *sulphides*. And, to this end, the sulphides are reproduced; the whole remaining alkaline sulphidic solution (556) being reprecipitated by an acid. If we employ *separative solvents*, we may choose between three (459), viz.: *ammonium carbonate*, dissolving **As<sub>2</sub>S<sub>3</sub>** and leaving the other sulphides; *hydrochloric acid*, leaving **As<sub>2</sub>S<sub>3</sub>** undissolved and dissolving the other two sulphides (500 e, and 542, last equation); and *alkali sulphites*, which dissolve **As<sub>2</sub>S<sub>3</sub>** and leave the antimony and tin undissolved. Neither one of these solvents effects a strict separation, and more exact and satisfactory results are obtained by Marsh's operation (463); receiving all the gas in solution of silver nitrate (506), and treating the residue in the generator for tin (535). This plan is the one given in the **Table** for the second group, Part III.

**559.** The separation of arsenic by ammonium carbonate, as a solvent, has been used in the following plan:

**Sulphides Precipitated from the  $(\text{NH}_4)_2\text{S}_2$  Solution:**  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}_2$ , (S), (556).

*Digest with Solution of Ammonium Carbonate, and Filter (457 d).*

<b>Residue:</b> $\text{SnS}_2$ , $\text{Sb}_2\text{S}_3$ , (S). <i>Dissolve in hot hydrochloric acid (542, 516).</i> <b>Solution:</b> $\text{SnCl}_4$ , $\text{SbCl}_3$ . <i>Treat with zinc and hydrochloric acid in presence of Platinum foil, in Marsh's apparatus (535).</i>		<b>Solution:</b> $(\text{NH}_4)_4\text{As}_2\text{S}_5 + (\text{NH}_4)_4\text{As}_2\text{O}_5$ <i>Precipitate by hydrochloric acid; filter; wash the precipitate and dissolve it by chlorine generated from a minute fragment of potassium chlorate and a little hydrochloric acid (459 e).</i> <i>Expel all free chlorine (463).</i>
<b>Deposit:</b> Sn, (Sb). <i>Dissolve by hydrochloric acid.</i> <b>Solution:</b> $\text{SnCl}_2$ . (Residue, Sb.) <i>Test by mercuric chloride (448 a).</i> <i>Examine by 545, etc.</i>	<b>Gas:</b> $\text{SbH}_3$ . (Test the spots, 466.) <i>Receive the gas in solution of silver nitrate. Dissolve the precipitate (<math>\text{Ag}_3\text{Sb}</math>) (506), and test by <math>\text{H}_2\text{S}</math>.</i> <i>Compare by 545.</i>	<b>Solution:</b> $\text{H}_3\text{AsO}_4$ <i>Apply Marsh's Test, as directed in 463, testing the spots (466); receiving the gas in solution of silver nitrate, and testing the resulting solution (467).</i> <i>Examine the original solution, as indicated in 545, and the text.</i>

The plan above given may be varied by separating antimony and tin by ammonium carbonate in fully oxidized solution, as follows: The  $\text{Sb}_2\text{S}_5$  and  $\text{SnS}_2$  are dissolved by nitro-hydrochloric acid, to obtain the antimony as metantimonic acid. The solution is then treated with excess of ammonium carbonate, in a vessel wide enough to allow the carbonic acid to escape without waste of the solution.

The diammonium dihydrogen metantimonate,  $(\text{NH}_4)_2\text{H}_2\text{Sb}_2\text{O}_7$ , is formed. Meanwhile the  $\text{SnCl}_4$  is fully precipitated as  $\text{SnH}_2\text{O}_3$  (equation in 540), and may be filtered out from the solution of metantimonate.

The liability of failure, in this mode of separating antimony and tin, lies in the non-formation of metantimonic acid by nitro-hydrochloric acid. The ordinary antimonious acid forms a less soluble ammonium salt, but this acid is not so likely to occur in dissolving as antimonious chloride,  $\text{SbCl}_3$ . Now, excess of ammonium carbonate does not redissolve the  $\text{Sb}_2\text{O}_3$  which it precipitates from  $\text{SbCl}_3$ , as stated in 499.

**560.** Separation of Arsenic from Sb, Sn, Bi, Cu, and Hg, by treatment of their sulphides with strong Nitric Acid—the resulting nitrates being decomposed by heat.\* The washed precipitate of sulphide is treated, in an evaporating-dish, with nitric acid of sp. gr. 1.2 or stronger, that which is brown by presence of nitrogen oxides being best, until brown vapors are no longer evolved. The mixture is then evaporated to dryness. If separation

\* VICTOR C. VAUGHAN: *Amer. Chem.*, vi. (1875) 41; vii. (1877), March.



from copper or bismuth is desired, the heat must be slowly increased (by use of a sand bath) to a temperature of  $400^{\circ}$  to  $600^{\circ}$  C., not reaching a red heat, and in all cases insuring the expulsion of all sulphuric and nitric acids. The residue is now digested with hot water (for about ten minutes), and filtered. **Solution:**  $\text{H}_3\text{AsO}_4$ . **Residue:**  $\text{Sb}_2\text{O}_3$  or  $\text{Sb}_2\text{O}_5$ ,  $\text{SnO}_2$ ,  $\text{CuO}$  and basic copper salt,  $\text{Bi}_2\text{O}_3$ ,  $\text{HgS}$ . If copper and bismuth are to be separated, the heat must be sufficient to vaporize sulphuric acid, which is necessarily formed. For separation of arsenic from antimony and tin, this is a convenient method, and gives exact results. The residue of antimony is soluble in nitro-hydrochloric acid; that of tin, slowly soluble in hot hydrochloric acid.

**561.** The solubility of arsenic sulphide (459 *d*), and the insolubility of sulphides of antimony and tin in solution of *acid sodium sulphite*, furnish a basis for the following:

**Plan for Separating Arsenic Sulphide by Acid-Sulphites, and Antimony and Tin Sulphides, by Nitric and Tartaric Acids.**

After precipitation of the solution of the thiosalts with dilute *hydrochloric acid* and some hydrosulphuric acid, and washing:

**Precipitate (a):**  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_5$ ,  $\text{SnS}_2$ , (free sulphur).

Transfer *precipitate (a)* to a test-tube or beaker, and digest at the boiling point, for some time, in a solution of *sodium acid sulphite* with free sulphurous acid. Filter, and wash the residue.

**Solution (b):**  $\text{NaAsO}_2$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ; ( $\text{NaHSO}_3$ ) (459 *d*).

**Residue (c):**  $\text{Sb}_2\text{S}_5$ ;  $\text{SnS}_2$  (free sulphur).

Acidulate *solution (b)* with *hydrochloric acid*: add *hydrosulphuric acid*, and digest, warm; if a precipitate occurs, treat it in an evaporating-dish with nitric acid; filter and wash from the excess of sulphur; concentrate the solution, and test it for **arsenic** by Bettendorf's method (468), or by reduction with cyanide (471).

Digest *residue (c)* with hot, *concentrated nitric acid* in an evaporating-dish, and expel the excess of acid.

**Product (d):**  $\text{Sb}_2\text{O}_5$ ;  $\text{H}_{10}\text{Sn}_5\text{O}_{15}$  (sulphur and  $\text{H}_2\text{SO}_4$ ) (494 *d*, 526 *d*).

Treat the *product (d)* with hot solution of *tartaric acid*, and filter.

**Solution (e):**  $\text{Sb}_2\text{O}_2\text{C}_4\text{H}_4\text{O}_6$ ; (excess of acids).—(496 *a*)

**Residue (f):**  $\text{H}_{10}\text{Sn}_5\text{O}_{15}$ , as metastannic acid (sulphur).

Test *solution (e)* with hydrosulphuric acid (and hydrochloric acid) for **antimony**; testing further by dissolving the sulphide, etc.

Fuse *residue (f)* with sodium carbonate and *cyanide*, on charcoal, and examine for tin (536). Dissolve in hydrochloric acid; test with mercuric chloride, etc.

**562.** If the *acid solution* of **As**, **Sb**, and **Sn**—prepared by dissolving the sulphides in hydrochloric acid with potassium chlorate—is treated with boiling **solution of sodium thiosulphate**, the arsenic and antimony are precipitated as sulphides (459 and 501), the tin left in solution.

The *sulphides* of **As** and **Sb**, so produced, may now be separated by hot solution of

sulphites with sulphurous acid, as directed for precipitate *a*, 561; leaving the arsenic in solution, and the antimony as residue.

We now have:

Solution (*a*):  $\text{SnCl}_4$ . (Precipitate by  $\text{H}_2\text{S}$ ; also reduce with **Zn** and test.)

Solution (*b*):  $\text{NaAsO}_2$ . (Treat as directed for solution *b*, 561.)

Residue (*c*):  $\text{Sb}_2\text{S}_5$ . (Dissolve in hydrochloric acid, and test.)

**563.** The separation of **As**, **Sb**, and **Sn**, by fusion with sodium salts and oxidizing agents, is indicated in 520. It will be seen, from the statements at the close of that paragraph, that when  $\text{SnO}_2$  is fused with sodium hydroxide, a stannate of sodium ( $\text{Na}_2\text{SnO}_3$ ) is formed, which dissolves in water; but when fused with sodium carbonate and nitrate (at a heat which does not convert the latter salt to caustic soda), it remains as stannic oxide, insoluble in water.

Now, the fusion of fully oxidized arsenic and antimony with sodium carbonate and nitrate (with or without caustic soda) converts both these elements into the (non-volatile) sodium arsenate and metantimonate— $\text{Na}_3\text{AsO}_4$  and  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ —the arsenate soluble, and the metantimonate insoluble, in cold water.

Hence, fusion of fully oxidized **As**, **Sb**, and **Sn** with sodium hydroxide, enables us to separate antimony from arsenic and tin; fusion, with sodium carbonate, etc., without sodium hydroxide, separating arsenic from antimony and tin.

The fusion with sodium hydroxide requires a silver or nickel crucible.

### Separation of fully oxidized Arsenic, Antimony, and Tin, by fusion with Sodium Carbonate and Nitrate, and Reduction.

The sulphides precipitated by hydrochloric acid from the solution of thio-salts are taken for oxidation.

Precipitate (*a*):  $\text{As}_2\text{S}_3$ ;  $\text{Sb}_2\text{S}_5$ ;  $\text{SnS}_2$  (sulphur).

Digest, in an evaporating dish, with hot *nitric acid*, in repeated portions, and evaporate to dryness at a gentle heat.

Residue (*b*):  $\text{H}_3\text{AsO}_4$ ;  $\text{Sb}_2\text{O}_5$ ;  $\text{H}_{10}\text{Sn}_5\text{O}_{15}$  (free sulphur).

Mix with one or two parts of *sodium carbonate*, and two or three parts of *sodium nitrate*; *fuse* (in a porcelain crucible), for some time, and until the mass is quiet, at a heat not much above the fusing point of the mass. Pour the fused mass upon a cold slab; pulverize, and digest in *cold water*. Filter.

Solution (*c*):  $\text{Na}_3\text{AsO}_4$  (sodium carbonate and nitrite).

Residue (*d*):  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ ;  $\text{SnO}_2$ .

Acidulate solution (*c*) with acetic acid, and test it with magnesia mixture, etc., for **arsenic**, according to 478, etc. The various precipitated arsenates may be collected, and with the remaining portion of solution (*c*), submitted to Marsh's Test.

Treat residue (*d*) with *concentrated hydrochloric acid*, hot, until dissolved. *Dilute* until the solution is sparingly acidulated and transfer to a platinum dish, or a porcelain dish with a piece of *platinum* foil (rinsing out any white residue which may have been precipitated by the water), and proceed to *reduce* antimony and tin, *with zinc*, according to 503.

Deposit (*e*): **Sb** (staining the platinum); **Sn** (not adherent).

Rinse the dark, spongy precipitate from the zinc with water, and remove the zinc. Treat the precipitate and the stained platinum with hot, moderately concentrated hydrochloric acid. Treat the stained platinum separately, first with hot nitric acid, then with concentrated solution of tartaric acid.

Solution (*f*):  $\text{SnCl}_2$ ;  $\text{ZnCl}_2$ . (Test for tin, with mercuric chloride.)

Solution (*g*):  $\text{Sb}_2\text{O}_3 \cdot \text{C}_4\text{H}_4\text{O}_6$ . (Obtain the sulphide; dissolve in solution of  $\text{K}_2\text{CO}_3$ —500 *d.*)

If with the fusion, as above, sodium hydroxide be added :

Solution (*e*):  $\text{Na}_3\text{AsO}_4$ ;  $\text{Na}_2\text{SnO}_3$  (sodium hydroxide, carbonate and nitrite).

Residue (*d*):  $\text{Na}_4\text{Sb}_2\text{O}_7$  and (by action of water)  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ .

Acidulate solution (*e*) with *sulphuric acid*, and expel all nitrous gas, and conduct Marsh's Test for **arsenic**; examining the residue for **tin**, according to 535.

Dissolve residue (*d*) with hydrochloric acid; obtain the sulphide of **antimony**; dissolve the latter, and test.

**564.** The **Second Portion** of the second-group bases—obtained as stated in 555, and washed as specified in 556—is dissolved in hot, moderately dilute *nitric acid*. Oxides of nitrogen pass off, instead of hydrogen sulphide; and sulphur is left, together with the black mercuric sulphide, if any mercury is present. The solution occurs mostly with evolution of **NO**, and essentially as shown for copper and lead, in equations 342 *a*, and 388 *a*. Traces of **HgS** may dissolve; and, if the nitric acid be strong and its action prolonged, more than traces of **PbSO<sub>4</sub>** (white) may be formed, and left insoluble with the mercury—according to equation *b*, 388. Some, or all, of the lead sulphate may be dissolved by the strong nitric acid; but, as the acid loses strength in the digestion and during filtration, it will precipitate from this solution. And it is even less soluble in *dilute* sulphuric acid, its precipitant, than in water.

The excess of nitric acid is mostly expelled by evaporation, and water is added, but not sufficient to precipitate bismuth (358); and if a white precipitate is seen to form on dilution, it is dissolved by sufficient nitric acid.

**565.** The solution is now tested, consecutively:

(*a*), with sulphuric acid (and alcohol) to precipitate lead;

(*b*), unless removed in first group, with hydrochloric acid to precipitate silver;

(*c*), with excess of ammonium hydroxide to precipitate bismuth, white (359),

to dissolve copper, blue (340),

and to dissolve cadmium, colorless (374).

Tests (*a*) and (*b*) are each made in a small portion of the material; if, by test (*a*), lead is detected, then lead is removed from the whole material by precipitation with sulphuric acid and filtration. The same course is pursued with test (*b*); and in ordinary analysis silver is never found in this group, being removed in the first group. This precaution provides against the addition of a large excess of mineral acids to the whole material, which will then be so greatly diluted by neutralizing with ammonium hy-

dioxide that test (c) is of no value. And in case lead (and silver) have to be removed, the filtrate should be evaporated to expel the excess of acid, then used for test (c).

**566.** Some analysts dissolve the sulphides, (2) 555, in concentrated nitric acid, then dilute and add dilute sulphuric acid (and alcohol) *before* filtration; **leaving the lead with the mercury— $\text{PbSO}_4$  with  $\text{HgS}$ .** This residue is then boiled with *ammonium acetate*, which dissolves the lead sulphate, as stated in 389, and leaves the black mercuric sulphide (with free sulphur) undissolved.

**567.** In any case, the addition of *alcohol* renders the sulphuric acid test for **lead** much more delicate (389); but the alcohol must be added very sparingly, and with a full knowledge that cupric and other sulphates are insoluble in alcohol, unless it be very dilute, and these salts may be precipitated by its free addition.

The formation of the yellow precipitate of *lead chromate*, from the white precipitate of sulphate (389), is a convenient confirmation. The solubility of the lead chromate in *fixed alkalis* distinguishes it from the yellow bismuth chromate (327), and the same reaction is a characteristic of the sulphate (see 549).

**568.** The precipitation by *water*, in this section of the group, is characteristic for **bismuth** (358). The *reduction* of the precipitated hydrate by sugar and fixed alkali, with black color (366), distinguishes bismuth from lead and from copper, the latter being thereby reduced with a reddish-brown color (346).

**569.** Owing to the waste of **copper** sulphide by ammonium sulphide, discussed in 557, a rigid analysis for this metal is most easily accomplished by examination of the original solution, or of the filtrate from the first group, by reduction with iron, or iron and platinum, according to 346.

The reduced copper may be dissolved by nitric acid, for further reactions.

**570.** The **Table** directs the test for **cadmium**, by hydrosulphuric acid, in the ammoniacal solution, which may contain copper or cadmium, or both. Now, both copper and cadmium are precipitated as sulphides in alkaline solutions (342 and 334); if the precipitate is yellow, it cannot contain much cupric sulphide; if it is black, it may consist largely of cadmium sulphide. But we have two agents capable of readily separating **CuS** from **CdS** (342):

Solution of potassium cyanide dissolves **CuS**, and leaves **CdS** undissolved. Hot dilute sulphuric acid dissolves **CdS**, and leaves **CuS** undissolved.

**571.** The separation of **mercury**, by the insolubility of its sulphide with nitric acid (555, portion 3) is generally satisfactory, but it is not rigorously exact. There is usually an excess of sulphur with it, but the color of **HgS** is intense enough to blacken a large quantity of sulphur. This pre-



precipitate may be treated with carbon disulphide to dissolve away the free sulphur; then dried, mixed with sodium carbonate, and sublimed in a small glass tube closed at one end (449), with good results.

The solution with chlorine is generally tested by *reduction*, most often with stannous chloride. Reduction requires, as a matter of course, that the excess of chlorine should first be expelled.

The test by *ammonium hydroxide* (433 and 443) is exceedingly delicate for mercury—in either class of combinations—though, of course, not characteristic to the eye. It may be used, in any solution, to confirm the absence of mercury.

## 572. Plan for separating the Bases without the use of Hydrosulphuric Acid or Ammonium Sulphide.\*

The solution (*a*) may contain salts of :

- I.—Pb, Ag, (Hg<sub>2</sub>)'' ;
- II.—Ca, Ba, Sr ;
- III.—NH<sub>4</sub>, Na, K ;
- IV.—As, Sb, Sn, Hg'', Cu, Cd, Bi ;
- V.—Fe, Cr, Al ;
- VI.—Mn, Mg, Co, Ni ;
- VII.—Zn.

Add *hydrochloric acid* to the solution (*a*) ; agitate, filter, and wash.

Precipitate (*b*) : (PbCl<sub>2</sub>) ; AgCl ; Hg<sub>2</sub>Cl<sub>2</sub>.

Solution (*c*) : Salts in solution (*a*), except Ag and (Hg<sub>2</sub>)''.

The *lead* in precipitate (*b*) is separated by *hot water* and filtration, then precipitated with sulphuric acid, etc. The *silver* is dissolved by *ammonium hydroxide*, and reprecipitated by nitric acid ; leaving the *mercury* as a black residue, insoluble in ammonium hydroxide, but soluble in nitro-hydrochloric acid.

The solution (*c*) is treated with excess of dilute *sulphuric acid* ; the precipitate filtered out and washed.

Precipitate (*d*) : CaSO<sub>4</sub> ; BaSO<sub>4</sub> ; SrSO<sub>4</sub> ; (PbSO<sub>4</sub>).

Solution (*e*) : Classes III., IV., V., VI., and VII., of solution (*a*).

From precipitate (*d*)—the *calcium* sulphate is dissolved by agitation with *cold water*, and then precipitated by ammonium *oxalate*. See further, for calcium, under filtrate (*k*). Then, the *lead* sulphate is dissolved out by solution of *ammonium tartrate* with ammonium hydroxide, the solution acidulated with acetic acid and precipitated by *chromate*. The residue—insoluble in water and in ammonium tartrate—contains the *barium* and *strontium* sulphates. [These may be separated by first transforming them into carbonates, by boiling with sodium carbonate, filtering, and washing out the sodium sulphate ; then dissolving the carbonates in *hydrochloric acid*, evaporating to dryness, digesting in *absolute alcohol*, and filtering. The residue of *barium* chloride, free from alcohol, dissolved in water, should be precipitated by solution of *strontium sulphate*. The alcohol solution (*strontium* chloride) may be tested for strontium with the *flame*.]

\* ZETTNOW : *Poggendorff's Annalen*, 130. p. 324 ; *Zeitsch. f. anal. Chem.*, VI (1867), 438 ; *Watts' Dictionary*, First Supplement, 124. Arranged in tabular form by H. C. BOLTON ; *Amer. Chem.*, III. (1873), 452.

Solution (e) is divided into a  $\frac{1}{4}$  part and a  $\frac{3}{4}$  part. The smaller part is tested for the **alkalies**, as follows:

*Ammonia* is detected in vapor, on adding excess of *solution of barium hydroxide*, and boiling. The barium is then removed by precipitation with ammonium carbonate (or dilute sulphuric acid), filtering and igniting the evaporated filtrate. The residue is examined for **potassium** and **sodium**, by *flame colors*, both with and without blue glass.

The  $\frac{3}{4}$  part of solution (e) has yet to be tested for classes IV., V., VI., and VII.: **As**, **Sb**, **Sn**, **Hg''**, **Cu**, **Cd**, **Bi**; **Fe**, **Cr**, **Al**; **Mn**, **Mg**, **Co**, **Ni**; **Zn**.

This portion of solution (e)—left with the excess of sulphuric acid from formation of precipitate (d)—is treated with *zinc* and a *piece of platinum foil in Marsh's apparatus*. The evolved gas is tested for arsenic and antimony—more perfectly by conducting it into solution of silver nitrate, and proceeding as elsewhere provided. The zinc will reduce the remaining metals of the fourth class.

Heat the generating flask ten or fifteen minutes, and filter.

Deposit (f): **Sb**, **Sn**, **Hg**, **Cu**, **Cd**, **Bi**.

Filtrate (g): **Fe**, **Cr**, **Al**; **Mn**, **Mg**, **Co**, **Ni**; **Zn** (as sulphates).

Deposit (f), well washed, is treated in an evaporating dish with *strong nitric acid*, and filtered.

Solution (h): Nitrates of **Hg**, **Bi**, **Cu**, and **Cd**.

Residue (i): (**Sb<sub>2</sub>O<sub>3</sub>**), **SnO<sub>2</sub>**.

Test half of solution (h) with *stannous chloride* for **Mercury**. To the other half add hydrochloric acid, and boil; then add *excess of sodium hydroxide*. The precipitated hydroxides of bismuth, copper, and cadmium are treated on the filter (after washing) with *ammonium hydroxide* and *ammonium chloride*. The **bismuth** is left undissolved; \* the **copper** and **cadmium** in their ammonia solutions. The copper is recognized by its color, and by precipitation with *ferrocyanide*, after acidulation. The cadmium is distinguished from copper by precipitation by *sodium hydroxide in the ammoniacal solution*.†

Residue (i) is washed, and boiled with *hydrochloric acid*, which dissolves the antimonic acid, and leaves the metastannic acid undissolved. The solution is tested with *platinum and zinc* for **antimony**. The residue is dissolved, with action of nascent hydrogen, by *hydrochloric acid with zinc*, and tested with *mercuric chloride* for **tin**.

Treat filtrate (g) with *nitric acid*, for oxidation. Test a small portion with *thiocyanate*, for **iron**. Treat the remaining portion with *barium carbonate* (after neutralizing with ammonia); digest for some time, and filter.‡

Precipitate (j): **Cr<sub>2</sub>(OH)<sub>6</sub>**, **Al<sub>2</sub>(OH)<sub>6</sub>**, with **Fe<sub>2</sub>(OH)<sub>6</sub>**, and excess of **BaCO<sub>3</sub>**.

Filtrate (k): **Mn**, **Mg**, **Co**, **Ni**; **Zn** (as sulphates).

Treat precipitate (j) with dilute sulphuric acid, to remove the barium, and filter. Boil the filtrate to expel carbonic anhydride; then boil with *excess of sodium hydroxide*, and digest with a little *potassium permanganate* to oxidize the chromium to chromate. Test a portion of this soda

\* The residue is dissolved in *hydrochloric acid*, and the solution treated with much *water*, for the more certain determination of **bismuth**.

† In case that much copper is present, the test for **cadmium** is better made as follows: The solution is strongly acidulated with *hydrochloric acid*, and boiled; then, while hot, treated with successive small additions of solution of *sodium thiosulphate*, to completion of the black precipitate, the liquid being milky with sulphur. After filtration, the filtrate is tested by sodium hydroxide for cadmium.

‡ If the presence of phosphoric acid is to be provided for, add sufficient *ferric chloride*, and digest before neutralizing and adding barium carbonate.

solution with *lead acetate* (after acidulation with acetic acid) for **chromium**. Treat another portion with *ammonium chloride* in excess for precipitation of **aluminium**.\*

From filtrate (*k*) remove the barium by adding a very slight excess of sulphuric acid, and filtering; then add *ammonium carbonate* in slight excess to precipitate **manganese**, and filter. Test a portion of the precipitate for manganese, by fusion with *sodium nitrate* and *carbonate*. Treat another portion for **calcium**, which escapes precipitate *d*, by adding ammonium hydrate to neutralize; then much *ammonium chloride*, and *ammonium oxalate*. To the filtrate, add *sodium phosphate* to precipitate **magnesium**, and filter. Evaporate the filtrate to dryness; it may contain cobalt and nickel. Dissolve it in hydrochloric acid, and add *potassium nitrite* and *acetic acid* and leave some hours to precipitate **cobalt**, and filter. To the filtrate, add *sodium hydroxide*, for the precipitation of **nickel**.

To test for **zinc** (*seventh class*), take a portion of solution (*e*)—or prepare it anew from the original solution by treatment, successively, with sulphuric and hydrochloric acids and filtration; and warm with *excess of sodium hydroxide*, and filter.† The filtrate (sodium zincate) is nearly neutralized with *ammonic carbonate*, and treated with *ammonic chloride* as long as ammonia escapes, and again filtered. The last filtrate is tested with *potassium ferrocyanide* for a precipitate of **zinc**.

## GOLD. Au = 196 155.

**573.** *Specific gravity*, 19.265 (MATTHIESSEN, 1860). *Melting point*, 1045° C. (4064° F.) (VIOLE, 1881). Valence, a monad in  $\text{Au}'_2\text{O}$  and in all aurous compounds. A triad in  $\text{Au}'''_2\text{O}_3$  and in all auric compounds.

**574. Occurrence.**—Gold is usually found native, but never perfectly pure, being always alloyed with silver, and occasionally also with other metals. It is found as gold-dust in alluvial sand, sometimes in nuggets, and sometimes disseminated in veins of quartz.

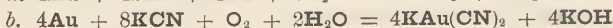
**575. Extraction.**—Three principal methods are employed. (1) Washing. Which consists in treating the well-powdered ore with a stream of water, the heavy gold settling to the bottom. (2) Amalgamation. Which consists in dissolving the gold in mercury and then separating it from the latter by distillation. (3) By fusing with metallic lead, which dissolves the gold, the liquid alloy settling to the bottom of the slag. The gold is afterward separated from the lead by cupellation. The silver is separated from the gold by dissolving it in nitric or sulphuric acid. Or the whole is dissolved in nitro-hydrochloric acid, and the gold precipitated in the metallic state by some reducing agent; ferrous sulphate being usually employed. Another method is to pass chlorine into the melted alloy. The silver chloride rises to the surface, while the chlorides of **Zn**, **Bi**, **Sb**, and **As** (if present) are volatilized, and the pure gold remains beneath. A layer of fused borax upon the surface prevents the silver chloride from volatilizing.

\* Manganese, and even other metals belonging in filtrate *k*, may be precipitated from their sulphates by barium carbonate, in absence of *sufficient* ammonium chloride.

† Zettnow directs to "boil" with the excess of sodium hydroxide, but this is liable to precipitate zinc.

**576. Properties.**—In malleability and ductility it surpasses all other metals. 282,000 gold leaves placed upon each other form a pile only one inch high. And one gramme may be drawn into a wire 3,240 meters in length. And one grain of gold will gild two miles of silver wire. It is slightly volatile at a very high temperature. According to WIEBE at 2240° C. (*Ber.*, 1879, 12, 791).

Gold is not tarnished or affected by air or water at any temperature, or by hydrosulphuric acid. Neither nitric nor hydrochloric acid attacks it under any conditions; but it is rapidly attacked in vapor or solution by **chlorine**, dissolving promptly in nitro-hydrochloric acid, as *auric chloride*,  $\text{AuCl}_3$ ; by **bromine**, dissolving in bromine water, as *auric bromide*,  $\text{AuBr}_3$ ; and by **iodine**; dissolving when finely divided in hydriodic acid by aid of the air and potassium iodide, as *potassium auric iodide*,  $\text{KIAuI}_3$  (a). **Cyanide** of potassium solution, with aid of the air, dissolves precipitated gold as *potassium aurocyanide*,  $\text{KAu(CN)}_2$  (b):



**577.** Gold forms two *oxides*: *aurous*,  $\text{Au}'_2\text{O}$ , and *auric*,  $\text{Au}''_2\text{O}_3$ ; but forms no stable oxy-salts. It forms the two classes of haloid salts, corresponding to the oxides. The *aurous chloride*,  $\text{AuCl}$ , and *other* aurous salts, are either insoluble in water or decomposed by water with partial solution and separation of gold,  $3\text{AuCl} = 2\text{Au} + \text{AuCl}_3$ .—The *auric chloride*,  $\text{AuCl}_3$ , and bromide, are soluble in water; the iodide decomposed by water, with precipitation of yellow aurous iodide; the sulphide insoluble in water. There are many double salts of gold and alkali metals, mostly soluble in water; double chlorides and iodides; aurocyanides, as  $\text{NH}_4\text{Au(CN)}_2$ , and aurieyanides, as  $\text{KAu(CN)}_4$ ; and a sodio-aurous thiosulphate,  $\text{Na}_3\text{Au(S}_2\text{O}_3)_2$ , soluble in water.

Gold is most readily **separated** and distinguished by reduction to the metallic state.

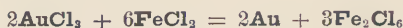
**578.** Fixed **alkali hydroxides** do not precipitate solution of auric chloride; ammonium hydroxide precipitates, in concentrated solution, a reddish-yellow *ammonia aurate*,  $(\text{NH}_3)_2\text{Au}_2\text{O}_3$ , “fulminating gold.”—**Hydrosulphuric acid**, whether hot or cold, dilute or concentrated, precipitates gold sulphide mixed with metallic gold or sulphur (V. SCHROTTER and PRIWOZNIK). The precipitates are insoluble in  $\text{HCl}$  and in  $\text{HNO}_3$ , even when hot, but soluble in nitro-hydrochloric acid. They are soluble both in yellow and colorless ammonium sulphide, and in the sulphides of the fixed alkalis. According to LEVOL the precipitate formed by  $\text{H}_2\text{S}$  is  $\text{Au}_2\text{S}_2$ . Soluble sulphides precipitate  $\text{Au}_2\text{S}_2$ ; soluble in yellow ammonium sulphide.

**Potassium iodide**, added in small portions to solution of auric chloride (so that the latter is constantly in excess where the two salts are in contact), and when equivalent proportions have been reached, gives a yellow precipitate of *aurous iodide*,  $\text{AuI}$ , insoluble in water, soluble in large excess of the reagent; the precipitate accompanied with separation of free iodine, brown, which is quickly soluble in small excess of the reagent as a colored solution [ $\text{AuCl}_3 + 4\text{KI} = \text{AuI} + 3\text{KCl} + \text{I}_2$  with  $\text{KI}$ ]. But, on gradually adding auric chloride to solution of potassic iodide, so that the



latter is in excess at the point of chemical change, there is first a dark-green solution of potassio-auric iodide,  $\text{KIAuI}_3$ ; then a dark-green precipitate of *auric iodide*,  $\text{AuI}_3$ , very instable, decomposed in pure water, more quickly by boiling; changed in the air to the yellow aurous iodide.

All **reducing agents** are oxidized by auric chloride, with precipitation of *gold*—at first of a brown to a violet color, acquiring, when triturated, the color and lustre which distinguish it in mass. The metals, and all lower oxides and salts, reduce gold. **Ferrous sulphate** forms it in brown precipitate; **stannous chloride** gives a purple precipitate, “purple of Cassius,”  $\text{Au}_2\text{O}$ , containing the oxides of tin:



**579.** Gold is reduced from many of its compounds by **light**, and from all of them by **heat**—its separation **in the dry way** being readily effected by fusion with such reagents as will make the material fusible. Very small proportions are collected in alloy with lead, by fusion; after which the lead is vaporized in “cupellation,” as described for silver.

**580.** Gold is separated, from its alloys with silver and base metals, by solution in **nitric acid**; the gold being left as a black-brown powder—together with platinum and oxides of antimony and tin. When the gold-silver or gold-copper has not over 20 p. c. gold, nitric acid of 20 p. c. disintegrates the alloy, and effects the separation; when the gold is over 25 p. c., silver or lead (three parts) must be added, by fusion, to the alloy before solution. (If gold-silver alloy contains 60 p. c. or more of silver, it is silver-color; if 30 p. c. silver, a light brass-color; if 2 p. c. silver, it is brass-color.)

If gold and other metals are obtained in solution by **nitro-hydrochloric acid**, leaving most of the silver as a residue, the noble metals can be precipitated by zinc or ferrous sulphate, and the *precipitate* of gold, silver, etc., treated with nitric acid, which will now dissolve out any proportion of silver not less than 15 p. c., to 85 p. c. of gold, and dissolve the baser metals. Concentrated **sulphuric acid** dissolves silver, and leaves gold.

**Oxalic acid** reduces gold from solution, not too strongly acid, slowly but completely. To the auric chloride, it is better to add both ammonium oxalate and oxalic acid. Platinum, palladium, and the second-group metals are not reduced by oxalic acid; hence, whenever the systematic analysis of a solution is made to include gold, this metal should be tested for and *removed by oxalic acid, before the first and second-group precipitations*.

**581. Estimation.**—Gold is always weighed in the metallic state, to which form it is reduced: (1) By ignition, if it contains no fixed acid; (2) by adding to the solution some reducing agent, usually  $\text{FeSO}_4$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , hydrate of chloral, or some easily oxidized metal, such as **Zn**, **Cd**, or **Mg**. Gold is also estimated volumetrically by  $\text{H}_2\text{C}_2\text{O}_4$  and the excess of  $\text{H}_2\text{C}_2\text{O}_4$  used, determined by  $\text{K}_2\text{Mn}_2\text{O}_8$ .

**582. Oxidation.**—Gold is reduced to the metallic state by very many reducing agents, among which may be mentioned the following : Pb, Ag, Hg, (Hg<sub>2</sub>)'', Sn, Sn'', As, As''', AsH<sub>3</sub>, Sb, Sb''', SbH<sub>3</sub>, Bi, Bi', Cu, (Cu<sub>2</sub>)'', Pd, Pt, Te, Fe, Fe'', Al, Co, Ni, (Cr<sub>2</sub>)<sup>vi</sup>, Zn, Mg, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, HNO<sub>2</sub>, P, H<sub>3</sub>PO<sub>2</sub>, H<sub>3</sub>PO<sub>3</sub>, PH<sub>3</sub>, H<sub>2</sub>SO<sub>3</sub>, and a great number of organic substances.

### PLATINUM. Pt = 194.415.

**583. Specific gravity**, 21.50 (DEVILLE and DEBRAY, 1875). *Melting point*, 1775° C. (3227° F.) (VIOLETTE, 1879). Valence, a dyad in Pt<sup>iv</sup>O, and in all platinous compounds; a tetrad in Pt<sup>iv</sup>O<sub>2</sub>, and in all platinic compounds.

**584. Occurrence.**—Found in nature only in the metallic state, generally alloyed with palladium, iridium, osmium, rhodium, ruthenium, etc. The Ural Mountains furnish the largest supply of platinum.

**585. Properties.**—Pure platinum is softer than silver, but it generally contains iridium, which hardens it and increases its elasticity. In ductility it is surpassed only by gold and silver. It is a tin-white metal, nearly as lustrous as silver, fusible in the oxy-hydrogen blow-pipe flame, by which it can be vaporized. It is obtained as a soot-black powder—"platinum-black"—by reduction from solution of alkali and alcohol; and as a gray, porous, slightly coherent mass—"platinum-sponge"—by ignition of ammonio-platinic chloride. Both these bodies are remarkable for adhesive power; and both, by strong compression, become compact, malleable, and lustrous, in the ordinary form of the metal. Platinum is not affected by air or water, at any temperature; is not sensibly tarnished by hydrosulphuric acid vapor or solution; and is not attacked at any temperature by nitric acid, hydrochloric acid, or sulphuric acid, but dissolves in nitrohydrochloric acid, to platinic chloride, less readily than gold.

**586. The Preservation of Platinum Vessels** requires that it be remembered: (1) That free chlorine and bromine attack platinum at ordinary temperatures (forming platinic chloride, bromide); and free sulphur, phosphorus, arsenic, selenium, and iodine, attack ignited platinum (forming platinous sulphide, platinic phosphide, platinum-arsenic alloy, platinic selenide, iodide). Hence, the fusion of sulphides, sulphates, and phosphates, with reducing agents, is detrimental or fatal to platinum crucibles. The ignition of organic substances containing phosphates acts as free phosphorus, in a slight degree.

The heating of ferric chloride, and the fusion of bromides, and iodides, act to some extent on platinum.

(2) The alkali hydroxides (not their carbonates) and the alkaline earths, especially baryta and lithia, with ignited platinum in the air, gradu-

ally corrode platinum (by formation of platinites :  $2\text{Pt} + 2\text{BaO} + \text{O}_2 = 2\text{BaO.PtO}$ ). Nickel crucibles are recommended for fusion with alkali hydroxides.

(3) All **metals which may be reduced in the fusion**—especially compounds of lead, bismuth, tin, and other metals easily reduced and melted—and all **metallic compounds with reducing agents** (including even alkalies and earths) form fusible alloys with ignited platinum. Mercury, lead, bismuth, tin, antimony, zinc, etc., are liable to be rapidly reduced, and *immediately to melt away platinum* in contact with them.

(4) **Silica with charcoal** (by formation of silicide of platinum) corrodes ignited platinum, though very slowly. Therefore, platinum crucibles should not be supported on charcoal in the furnace, but in a bed of magnesia, in an outer crucible of clay. Over the flame, the best support is the triangle of platinum wire.

(5) The tarnish of the gas-flame increases far more rapidly upon the already tarnished surface of platinum—going on to corrosion and cracking. The surface should be kept polished—preferably by gentle rubbing with moist *sea-sand* (the grains of which are perfectly rounded, and *do not scratch* the metal). Platinum surfaces are also **cleansed** by fusing *borax* upon them, and by digestion with nitric acid.

**587.** Platinum forms two **oxides**, platinous oxide,  $\text{Pt}''\text{O}$ , and platinic oxide,  $\text{Pt}'''\text{O}_2$ —both of which represent corresponding classes of oxy salts and haloid salts. The oxy-salts are instable.—None of the **platinous** compounds are permanently **soluble** in pure water; the chloride is soluble in hydrochloric acid, the sulphate in water acidulated with sulphuric acid.—**Platinic chloride** ( $\text{PtCl}_4$ ) and bromide, all the platineyanides (as  $\text{PbPt}(\text{CN})_6$ ), and the platinocyanides of the metals of the alkalies and alkaline earths (as  $\text{K}_2\text{Pt}(\text{CN})_4$ ), are **soluble** in water. The platinous and platinic nitrates are soluble in water, but easily decomposed by it, with the precipitation of basic salts. The larger number of the *metallo-platinic chlorides* or “chloroplatinates” are soluble in water, including those with sodium [ $\text{Na}_2\text{PtCl}_6$  or  $(\text{NaCl})_2\text{PtCl}_4$ ], barium, strontium, magnesium, zinc, aluminium, copper; and those with potassium, and ammonium, are sparingly soluble in water, and owe their analytical importance as complete precipitates to their insolubility in alcohol. Of the *metallo-platinous chlorides* (the “chloroplatinites”)—those with sodium, [ $\text{Na}_2\text{PtCl}_4$ ], and barium, are soluble; zinc, potassium, and ammonium, sparingly soluble; lead and silver, insoluble in water. **Platinic sulphate**,  $\text{Pt}(\text{SO}_4)_2$ , is soluble in water.

**588. Platinous chloride**,  $\text{PtCl}_2$ , is a greenish-brown powder, soluble in hydrochloric acid without change, as a dark-brown solution, which remains platinous if protected from the air, but becomes platinic in contact with the air. The purely platinous chloride solution is precipitated by **potassium hydroxide** and sodium hydroxide as *platinous hydroxide*,  $\text{Pt}(\text{OH})_2$ , dark-brown, soluble in excess, as alkali platinite,  $\text{K}_2\text{PtO}_2$ , etc.; from which alkaline solutions, alcohol precipitates “platinum black” (585).—**Ammonium hydroxide** gives a green crystalline precipitate of *platino-diammonium chloride*,  $\text{N}_2\text{H}_6\text{PtCl}_2$ , insoluble in cold water and in alcohol (compare 433). **Hydrosulphuric acid** very slowly precipitates *platinous sulphide*,  $\text{PtS}$ , black, sparingly soluble in water, not affected by acids, sparingly **soluble by ammonium sulphide**.—**Iodide** of potassium slowly precipitates *platinous iodide*,  $\text{PtI}_2$ , red-brown to black.—Oxalic acid produces no change; **ferrous sulphate** (slowly), and **zinc** (quickly), reduce the *metal*.

**589. Platinic Chloride,  $\text{PtCl}_4$ ,** is a brown-red solid, dissolving in water, or alcohol, as a reddish-yellow solution, permanent in the air.—**Potassium hydroxide**, and **ammonium hydroxide**, give, in solutions not very dilute, a yellow crystalline precipitate, as *potassium platinic chloride*, or potassium chloroplatinate,  $\text{K}_2\text{PtCl}_6$ , etc., slightly soluble in water, insoluble in alcohol, soluble in excess of the alkalies, and reprecipitated by hydrochloric acid. **Chlorides** of potassium and ammonium give the precipitate, the most nearly complete. **Carbonates** of potassium and ammonium form the same precipitates, insoluble in excess. Sodium carbonate gives no precipitate. **Sodium hydroxide** slowly precipitates, in moderately concentrated solutions, after warming, the (brownish-yellow) sodium platinate,  $\text{Na}_2\text{PtO}_3$ .—**Potassium iodide** colors the solution brown-red, and precipitates the black *platinic iodide*,  $\text{PtI}_4$ ; with excess of the reagent, forming the sparingly soluble *potassium platinic iodide*,  $\text{K}_2\text{PtI}_6$ , brown. Sodium iodide the same.—**Hydrosulphuric acid**, and ammonium sulphide, slowly precipitate the black *platinic sulphide*,  $\text{PtS}_2$ , slightly soluble in water, soluble by chlorine, and soluble in **ammonium sulphide**, as ammonium *sulphoplatinate*; sodium sulphoplatinate is likewise soluble, reprecipitated by acids. Phosphates form no precipitate. **Reduction** is not effected by oxalic acid (distinction from gold); is slowly accomplished by **ferrous sulphate**, and rapidly by **zinc**; also by **chloral hydrate**, and excess of **alkali** with heat (formiate); the reduced metal being, in each case, in black powder.—By the reducing **blow-pipe flame**, the compounds of platinum are reduced to *spongy platinum*.

**590. Estimation.**—Platinum is invariably weighed in the metallic state. It is brought to this condition: (1) By simple ignition; (2) by precipitation as  $(\text{NH}_4)_2\text{PtCl}_6$ ,  $\text{K}_2\text{PtCl}_6$ , or  $\text{PtS}_2$  and ignition; (3) by reduction, using **Zn**, **Mg**, or  $\text{FeSO}_4$ .

**591. Oxidation.**—Solutions of platinum are reduced to the metallic state by the following metals: **Pb**, **Ag**, **Hg**, **Sn**, (**Sn''** to **Pt''**), **Bi**, **Cu**, **Cd**, **Zn**, **Fe**, **Fe''**, **Co**, and **Ni**. Very many organic substances reduce platinum compounds to the metallic state.

#### PALLADIUM. $\text{Pd} = 105.737$ .

**592. Specific gravity**, 11.4 (DEVILLE and DEBRAY, 1859). *Melting point*,  $1500^\circ \text{C}$ . ( $2732^\circ \text{F}$ .) (VIOLE, 1878). Valence, a dyad in  $\text{Pd}''\text{O}$  and in all palladous compounds. A tetrad in  $\text{Pd}'''\text{O}_3$ , and in all palladic compounds. Found in platinum ores.

**593. Properties.**—Spongy palladium absorbs 935 times its volume of hydrogen, and still retains 600 volumes at  $100^\circ \text{C}$ . At very high temperatures the whole of the hydrogen is given off. The absorbed hydrogen acts in some respects like nascent hydrogen; reducing mercuric chloride to



metallic mercury, etc. Palladium is a white metal, more lustrous than platinum, with which it is classed, in accordance with its general properties. It is, however, a little more fusible and volatile (in the oxyhydrogen flame), and much more oxidizable than platinum. In the air, it is little tarnished at ordinary temperatures, but at a red heat it covers with oxide.—It is slightly attacked by boiling hydrochloric or sulphuric acid; dissolves in nitric acid, with formation of palladous nitrate, and if in the cold, with separation of nitrous acid, which remains in solution; more readily in nitro-hydrochloric acid, as palladic chloride,  $\text{PdCl}_4$ . It is blackened by alcoholic solution of iodine (distinction from platinum).

594. Palladium forms one stable oxide, palladous,  $\text{PdO}$ , and two chlorides, palladous,  $\text{PdCl}_2$ , and palladic,  $\text{PdCl}_4$ . The latter is the most stable of the palladic combinations, but is reduced to palladous chloride by boiling in water, and by dilution with much cold water.

Palladous chloride is readily soluble in water with a brownish-red color; with metallic chlorides, it forms double chlorides, as potassio-palladous chloride,  $\text{K}_2\text{PdCl}_4$ , all of which are soluble in water.—Palladous iodide is insoluble in water, alcohol, or ether; insoluble in dilute hydrochloric acid or hydriodic acid; slightly soluble by iodides and by chlorides.—Palladous nitrate,  $\text{Pd}(\text{NO}_3)_2$ , is soluble in water with free nitric acid; the solution being decomposed by dilution, evaporation, or by standing, with precipitation of variable basic nitrates. Palladous sulphate,  $\text{PdSO}_4$ , dissolves in water, but decomposes in solution on standing.

The instable palladic chloride, brown-black in solution, forms double chlorides with the metals—as calcium palladic chloride,  $\text{CaPdCl}_6$ —these being mostly stable in water, and mostly soluble in water and in alcohol. The potassium palladic chloride (red), as an exception, is slightly soluble in water and insoluble in alcohol, but partially decomposed by both solvents.

595. Palladous Chloride is precipitated by potassium hydroxide or sodium hydroxide; as brown basic salt or as brown palladous hydrate,  $\text{Pd}(\text{OH})_2$ , soluble in excess of the hot reagents. Ammonium hydroxide gives a flesh-red precipitate of palladio-diammonium chloride,  $\text{N}_2\text{H}_6\text{PdCl}_2$ . The flesh-red precipitate is soluble in excess of the ammonia, and from this solution reprecipitated by hydrochloric acid, with a yellow color. The fixed alkali carbonates precipitate the hydroxide; ammonium carbonate acts like the hydroxide.—Hydrosulphuric acid and sulphides precipitate the dark-brown palladous sulphide,  $\text{PdS}$ , insoluble in the ammonium sulphides, soluble in nitro-hydrochloric acid.—Potassium iodide precipitates palladous iodide,  $\text{PdI}_2$ , black, visible in 500,000 parts of the solution, with the slight solubilities stated in 594, an important separation of iodine from bromine. In very dilute solutions, only a color is produced, or the precipitate separates after warming. At a red heat, the precipitate is decomposed. Potassium cyanide precipitates palladous cyanide,  $\text{Pd}(\text{CN})_2$ , white, soluble in excess of the reagent.—Chloride of potassium precipitates, from highly concentrated solutions, the golden yellow, crystalline, potassium palladous chloride,  $\text{K}_2\text{PdCl}_6$  (594). Phosphates give a brown precipitate.

Palladous nitrate gives most of the above reactions; no precipitate with ammonia, and a less complete precipitate with iodides.

596. Palladium is reduced, in dark-colored precipitate, from all compounds in solution, by sulphurous acid, stannous chloride, phosphorus, and all the metals which precipitate silver. Ferrous sulphate reduces palladium from its nitrate, not from its chlo-

ride. Alcohol, at boiling heat, reduces it ; oxalic acid does not (distinction from gold).—Nearly all its compounds are reduced by heat, before the blow-pipe, to a “sponge.” If this be held in the inner flame of an alcohol-lamp, it absorbs carbon at a heat below redness ; if then removed from the flame, it glows vividly in the air, till the carbon is all burnt away (distinction from platinum).

**597. Estimation.**—(1) As metallic palladium, to which state it is reduced by mercuric cyanide or potassium formate ; it is then ignited, first in the air and then in hydrogen gas. (2) As  $\text{K}_2\text{PdCl}_6$ . Evaporate the solution of palladic chloride with potassium chloride and nitric acid to dryness, and treat the mass when cold with alcohol of .833 sp. gr., in which the double salt is insoluble. Collect on a weighed filter, dry at  $100^\circ \text{C}$ ., and weigh.

### MOLYBDENUM. $\text{Mo} = 95.52\%$ .

**598. Specific gravity**, 8.56 (LOUGHLIN, 1868). Valence, a dyad in  $\text{Mo}''\text{O}$  and in  $\text{Mo}''\text{Cl}_2$  ; a triad in  $\text{Mo}'''_2\text{O}_3$  and in  $\text{Mo}'''_2\text{Cl}_6$  ; a tetrad in  $\text{Mo}^{\text{IV}}\text{O}_2$  and in  $\text{Mo}^{\text{IV}}\text{Cl}_4$  ; a hexad in  $\text{Mo}^{\text{VI}}\text{O}_3$  and in molybdates.

**599. Occurrence.**—Not found native. But occurs chiefly as molybdenite,  $\text{MoS}_2$ , as an oxide in molybdenum ochre,  $\text{MoO}_3$ , and as wulfenite,  $\text{PbMoO}_4$ . The metal is reduced from its oxides by heating with carbon, or in a current of hydrogen.

**600. Properties.**—It is a silver-white, hard and brittle metal, fusible at the highest furnace heat. It is not oxidized in the air at ordinary temperatures ; but when slowly heated, it gains a brownish-yellow, then a blue tarnish ; and at a higher heat, it burns to  $\text{MoO}_3$ . It is oxidized by water vapor at a red heat. It is quickly dissolved by nitric acid, as molybdic anhydride ( $\text{MoO}_3$ ), with evolution of nitric oxide ; slowly by hot, strong sulphuric acid, with liberation of sulphurous anhydride. Molybdenum forms three classes of compounds, viz., *molybdous oxide* (sometimes called hypomolybdous oxide),  $\text{Mo}''\text{O}$  ; chloride,  $\text{MoCl}_2$ , and other molybdous salts ; *molybdic oxide* (sometimes called molybdous oxide),  $\text{Mo}'''_2\text{O}_3$  ; chloride,  $\text{MoCl}_4$ , and corresponding salts ; and molybdic *anhydride*,  $\text{Mo}^{\text{VI}}\text{O}_3$ , which combines with bases, to form stable molybdates—also feebly unites with strong acids. Each of these classes includes stable salts ; the two bases are converted into molybdic acid or molybdates by strong oxidizing agents ; while molybdates are reducible to one or the other of the bases by deoxidizing agents.

**601.** The *molybdous* salts are not generally very permanent in solution. The chloride is soluble (in dilute hydrochloric acid ?) ; the bromide and iodide decomposed in water to oxybromide and oxyiodide ; the sulphate decomposed by water to a soluble and an insoluble salt ; the nitrate soluble in water. The solutions are dark-brown and opaque.

Water **dissolves** the tetrachloride, bromide (yellow-brown solution), iodide (red solution), nitrate and  $\text{Mo}(\text{SO}_4)_2$  (reddish-brown solutions).

Molybdic *anhydride* is very sparingly **soluble** in water (800 parts). It does not form an acid in the solid state. The normal *molybdates* of the alkali metals (as  $\text{K}_2\text{MoO}_4$ ) are soluble, of the remaining metals insoluble in water. The molybdenum trisulphate,  $\text{Mo}(\text{SO}_4)_3$ , and molybdenum hexa-chloride,  $\text{MoCl}_6$ , are soluble in water; the corresponding nitrate,  $\text{Mo}(\text{NO}_3)_6$ , soluble in dilute nitric acid.

**Molybdous** salts, as  $\text{Mo}(\text{NO}_3)_2$ , with **alkali hydroxide** and **carbonates**, precipitate the dark-brown *molybdous hydroxide*, becoming *blue* in the **air** by oxidation to molybdic molybdate,  $\text{Mo}(\text{MoO}_4)_2$  and  $\text{Mo}_2\text{O}_5$ . The hydroxide is insoluble in alkalies, sparingly soluble in alkali carbonates, readily soluble in alkali hydrogen carbonates. With **hydrosulphuric acid** and **sulphides**, a brown precipitate of *molybdous sulphide*,  $\text{MoS}$ , **soluble** in ammonium sulphide.

**602.** Molybdic salts, as  $\text{MoCl}_4$ , with **alkali hydroxides** and **sulphides**, give reactions corresponding with molybdous salts, and likewise turn *blue* in the **air**, by formation of intermediate oxides. The precipitated hydroxide is reddish-brown; it dissolves in alkali carbonates by formation of alkali molybdates. **Zinc** precipitates *molybdous hydroxide*, by reduction.

**603.** Molybdic **Anhydride** is a white powder, or is in needle-form crystals, turning yellow when hot and again white on cooling; melting at a red and vaporizing at a white heat. It is soluble by acids, and by alkali-hydroxides, especially ammonia, in formation of molybdates.

Water solutions of **MOLYBDATES**, with acids, precipitate molybdic anhydride,  $\text{MoO}_3$ , white, soluble in excess of the acids.\* **Hydrosulphuric acid** colors the molybdate in neutral or alkaline solutions, yellow to brown, without precipitation; but from the acid solutions it precipitates the brown  $\text{MoS}_2$ , *sulphomolybdic acid*, the supernatant liquid appearing blue. The precipitate is **soluble** in ammonium sulphide, better when hot and not too concentrated, as ammonium thiomolybdate,  $(\text{NH}_4)_2\text{MoS}_4$ , from which acids reprecipitate  $\text{MoS}_3$ .

**604.** Tribasic **phosphoric acid** and its salts precipitate, from strong nitric acid solutions of ammonium molybdate, somewhat slowly and on warming, *ammonium phosphomolybdate*, yellow, of variable composition, soluble in ammonia and other alkalies, sparingly soluble in excess of the phosphate. Hydrochloric acid may be used instead of nitric. The *sodium phosphomolybdate* is soluble in water, and precipitates ammonium from its salts; also, it precipitates the alkaloids—for which reaction it has some importance as a reagent.†

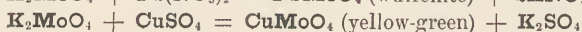
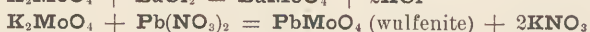
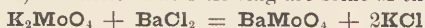
\* In making the solution of molybdate with nitric acid, used as a reagent, the slightly alkaline solution of the molybdate is poured into the nitric acid, slowly, with stirring.

† *Sodium Phosphomolybdate*—Sonnenschein's reagent for acid solutions of alkaloids—is prepared as follows: The yellow precipitate formed on mixing acid solutions of ammonium molybdate and sodium phosphate—the ammonium phosphomolybdate—is well washed, suspended in water, and heated with sodium carbonate until completely dissolved. The solution is evaporated to dryness, and the residue gently ignited till all ammonia is expelled, sodium being substituted for ammonium. If blackening occurs, from reduction of molybdenum, the residue is moistened with nitric acid, and heated again. It is then dissolved with water and nitric acid to strong acidulation; the solution being made ten parts to one part of residue. It must be kept from contact with vapor of ammonia, both during the preparation and when preserved for use.

Arsenic acid and **arsenates** give the same reaction ; *ammonium arsenomolybdate* being formed.

Recent molybdic anhydride, well washed (with alcohol and then water), on digestion with aqueous phosphoric acid, forms a lemon-yellow salt, insoluble in water, but slowly soluble in excess of the hot phosphoric acid, as acid permolybdic phosphate or *phosphomolybdic acid*. It is soluble in alcohol as well as in water ; the solution giving, with ammonia and with alkaloids, the yellow precipitate of ammonium phosphomolybdate, etc.

**605.** The alkaline solutions—normal molybdates of the alkali metals—give, with all **non-alkali salts**, precipitates of non-alkali molybdates, the latter being insoluble (or sparingly soluble) in water. The following are some of the reactions giving precipitates:



**606. Reducing agents** convert molybdic acid either into the *blue* intermediate oxides, or, by further deoxidation, into the *black* molybdous oxide, **MoO**. In the (hydrochloric) acid solutions of molybdic acid, the blue or black oxide formed by reduction, will be held in solution with a blue or brown color. Nitric acidulation is, of course, incompatible with the reduction. Certain reducing agents act as follows :

**Ferrous salts** (in the hydrochloric acid solution) give the *blue* oxide solution. **Cane sugar**, in the feebly acid boiling solution, forms the *blue* color—seen better after dilution ; a delicate test. **Stannous chloride** forms first the *blue*, then the *brown*, or the *greenish-brown* to black-brown, solution of both the intermediate oxide and the molybdous oxide. **Zinc** gives the *blue*, then *green*, then *brown* color, by progressive reduction. Formic and oxalic acids do not react.—Dry molybdates, heated on platinum foil with concentrated sulphuric acid to vaporization of the latter, form, on cooling in the air, a *blue* mass—a very delicate test.\*

**607.** With microcosmic salt, in the outer blow-pipe flame, all compounds of molybdenum give a bead which is greenish while hot, and colorless on cooling ; in the inner flame, a clear green bead. With borax, in the outer flame, a bead, yellow while hot, and colorless on cooling ; in the inner flame, a brown bead, opaque if strongly saturated (molybdous oxide). On charcoal, in the outer flame, molybdic anhydride is vaporized as a white incrustation ; in the inner flame (better with sodium carbonate), metallic molybdenum is obtained as a gray powder, separated from the mass by levigation.

**608. Estimation.**—(1) Molybdic anhydride and ammonium molybdate may be reduced to the dioxide by heating in a current of hydrogen gas.

\* A solution of 1 milligram of sodium (or ammonium) molybdate in 1 c.c. of concentrated sulphuric acid (about 1 part to 1,840 parts) is in use as **FRÉHDE'S** Reagent for alkaloids. The molybdenum in this solution, which must be freshly prepared for use each time, is reduced by very many organic substances ; and with a large number of alkaloids, it gives distinctive colors, blue, red, brown, and yellow.



The heat must not be permitted to rise above dull redness. Or the temperature *may* rise to a white heat, which reduces it to the metallic state, in which form it is weighed. (2) Lead acetate is added to the alkali molybdate, the precipitate washed in hot water, and after ignition weighed as  $\text{PbMoO}_4$ . (3) Volumetrically. The molybdic acid is treated with zinc and  $\text{HCl}$ , which converts it into  $\text{Mo}_2\text{Cl}_6$ . This is converted into molybdic acid again by standard solution of potassium permanganate.

#### GERMANIUM. $\text{Ge} = 72.32$ .

**609.**—*Specific gravity*, 5.469 (WINKLER, 1886). *Melting point*,  $900^\circ \text{C}$ . ( $1652^\circ \text{F}$ .) (WINKLER, 1886). Valence, a dyad in  $\text{Ge}''\text{O}$ , and in all germanous salts; a tetrad in  $\text{Ge}^{\text{IV}}\text{O}_2$ , and in all germanic salts. Found in argyrodite. A white, lustrous metal, brittle and easily powdered. It dissolves in  $\text{H}_2\text{SO}_4$ , not in  $\text{HCl}$ .  $\text{HNO}_3$  converts it into white  $\text{GeO}_2$ .

It forms two series of compounds, the germanous and the germanic.  $\text{GeCl}_2$  is formed by passing  $\text{HCl}$  over the heated metal, and is a colorless, fuming liquid, boiling at  $72^\circ \text{C}$ .

$\text{GeCl}_4$ , formed by the direct union of its elements, is also a liquid boiling at  $86^\circ \text{C}$ . It fumes in the air, and is decomposed by water.  $\text{GeO}$  is formed by treating  $\text{GeCl}_2$  with  $\text{KOH}$ , and heating the precipitate in a current of  $\text{CO}_2$ .  $\text{GeO}_2$  is formed when the metal burns in oxygen. It is white, and sparingly soluble in water, from which it may be crystallized. It acts as an oxide toward stronger bases. When  $\text{GeCl}_4$  is treated with  $\text{H}_2\text{S}$ ,  $\text{GeS}_2$  is precipitated. It is somewhat soluble in water, unless  $\text{HCl}$  is present. It dissolves in alkali sulphides. Heating it in hydrogen gas converts it into  $\text{GeS}$ .  $\text{GeS}$  is soluble in  $\text{KOH}$ , which converts it into germanium and  $\text{GeS}_2$ . For description of other germanium compounds see *Jr. Prakt. Chem.*, 1886, (2), 34, 177. Also other articles in same journal by C. WINKLER.

#### NORWEGIUM. $\text{Ng} = 218.93$ ?

**610.**—Discovered by DAHLL in a specimen of Norwegian nickel glance. *Specific gravity*, 9.441. *Melting point*,  $254^\circ \text{C}$ . Chemically it resembles bismuth. Its chloride is precipitated by water, forming an oxychloride. The oxide (probably  $\text{Ng}_2\text{O}_3$ ) is fusible, and gives, with the blow-pipe, a metallic incrustation. But unlike bismuth, its hydroxide is soluble in both the alkali hydroxides and alkali carbonates.

## 611. Reactions of Ruthenium, Iridium, Rhodium, and Osmium.

In solution as	$\text{Ru}_2\text{Cl}_6$ , orange.	$(\text{NaCl})_2\text{IrCl}_4$ , black.	$\text{K}_3\text{Rh}(\text{SO}_4)_3$ , rose-colored.	$\text{H}_2\text{OsO}_4$ .
$\text{H}_2\text{S}$ , in acid sol.	$\text{Ru}_2\text{S}_3$ , brown, formed slowly, with blue sol.	$\text{Ir}_2\text{S}_3 + \text{S}$ , brown.	$\text{Rh}_2\text{S}_3$ , brown, sol. in hot nitric acid.	Pre. $\text{OsS}_4$ , black.
$(\text{NH}_4)_2\text{S}_2$ , in excess.	Solution formed with difficulty.	Solution.	Precipitate.	Pre. $\text{OsS}_4$ , black.
$\text{KOH}$ or $\text{NaOH}$ , in excess.	$\text{Ru}_2(\text{OH})_6$ , black.	Brown-black pre., turning blue.	Solution, pre. by alcohol.	.....
$\text{SnCl}_2$ .	.....	$(\text{NaCl})_6\text{Ir}_2\text{Cl}_6$ .	.....	Pre. brown.
$\text{Zn}$ .	Pre., metallic $\text{Ru}$ .	$\text{Ir}$ , black.	$\text{Rh}$ , black.	$\text{Os}$ .
$\text{KNO}_3$ .	Pre., sol. in excess, turned to dark red by $(\text{NH}_4)_2\text{S}$ .	$\text{Ir}(\text{OH})_4 + \text{KNO}_3$ , boiled with $\text{SO}_2$ , green pre.	Pre., orange.	Pre. $\text{K}_2\text{OsO}_4$ .
	(1)	(2)	(3)	(4)

(1) **Potassium** thiocyanate, in absence of other platinum metals, slowly forms a *red color*, turning to violet when boiled.

(2) The metal is insoluble in all **acids**. After fusion with sodium hydroxide and oxidizing agents, it dissolves by nitro-hydrochloric acid.

(3) The metal is insoluble in all acids; but by fusion with potassium hydrogen sulphate, forms the soluble salt above taken.

(4) The metal vaporizes at white heat, and burns to  $\text{OsO}_4$ , an acidulous anhydride, having an irritating and offensive odor, and forming instable *osmates* of great oxidizing power. Osmates separate iodine from iodides, decolorize indigo solution, and, with **sulphites**, give a deep violet color or blue precipitate.

## 612. Reactions of Tellurium, Selenium, and Tungsten.

In solution as	$\text{K}_2\text{TeO}_3$ .	$\text{K}_2\text{TeO}_4$ .	$\text{Na}_2\text{SeO}_3$ .	$\text{Na}_2\text{SeO}_4$ .	$\text{Na}_2\text{WO}_4$ .
$\text{H}_2\text{S}$ in acid sol.	$\text{TeS}_2$ , brown,	.....	$\text{SeS}_2$ .	.....	Blue solution, $\text{Na}_2\text{WS}_4$ .
$(\text{NH}_4)_2\text{S}_2$ , excess.	No pre.	.....	No pre.	.....	No pre.
$\text{HCl}$ .	$\text{H}_2\text{TeO}_3$ , white pre.	Boiled, $\text{H}_2\text{TeO}_3$ , and $\text{Cl}$ .	No pre.	Boiled, $\text{H}_2\text{SeO}_3$ , and $\text{Cl}$ .	$\text{H}_2\text{WO}_4$ , white pre., then yellow.
$\text{SnCl}_2$ .	$\text{Te}$ , black.	.....	$\text{Se}$ , red.	.....	Yellow pre., heated with $\text{HCl}$ , blue.
<b>Fusion on Ch.</b> <b>with <math>\text{Na}_2\text{CO}_3</math>.</b>	$\text{Na}_2\text{Te}$ , staining $\text{Ag}$ , and with acids giving $\text{H}_2\text{Te}$ , having odor of $\text{H}_2\text{S}$ , and dissolving red.	(2)	$\text{Na}_2\text{Se}$ , staining $\text{Ag}$ , and with acids giving $\text{H}_2\text{Se}$ , of fetid odor, soluble in water.	(4)	$\text{W}$ , black.
	(1)	(2)	(3)	(4)	(5)

(1) The *tellurites* of the alkali and alkaline earthy metals are soluble in water, the other tellurites insoluble.

(2) The *tellurates* of the alkali metals, alone, are soluble in water.

(3) Except those of the alkali metals, the *selenites* are insoluble in water.

(4) Lead, barium, strontium, and calcium *selenates* are insoluble in water; other selenates, soluble. Barium selenate, insoluble in **HCl**.

(5) Of the *tungstates*, only those of the alkali bases dissolve in water.

## PART II.

### THE NON-METALS.

**613. VALENCE AND NEGATIVE BONDS.**—A Bond is a measure of oxidation. Its use in this work is independent of structural formulæ.

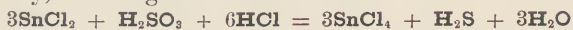
Oxidation is an increase of bonds. Reduction is a decrease of bonds. Formerly, oxidation was understood to mean an increase in oxygen. But the use of the word in that restricted sense has been completely abandoned.

One substance is said to oxidize another, when it transfers the whole or a part of its bonds to that other substance.

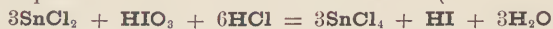
One substance is said to reduce another, when it receives the whole or a part of the bonds of that other substance.

When oxidation occurs, all of the bonds lost by the oxidizing agent are gained by the reducing agent. No bonds are annihilated. To conceive of such destruction would be a mathematical absurdity.

If the indestructibility of bonds is established, then the existence of negative bonds becomes a mathematical necessity. The bonds of free elements must be expressed by zero. That is, they either have no bonds, or, if they have any, their algebraic sum is zero.



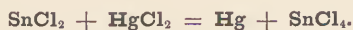
In this equation every one will admit that the three atoms of tin gain six bonds; the bonds of the sulphur in the  $\text{H}_2\text{SO}_3$  have then been diminished by six; that is, it has given up six bonds to the tin, and having only four in the first place must now have minus two. ( $4 - 6 = -2$ ).



Here also the three atoms of tin gain six bonds, and these are furnished by the iodine of the  $\text{HIO}_3$ . It has five in the first place, and being diminished by six, has one negative bond remaining ( $5 - 6 = -1$ ). In other words, unless we deny that iodine has five bonds in  $\text{HIO}_3$ , we must admit that it has one negative bond in  $\text{HI}$  (written  $\text{H}^+\text{T}'$ ).



In this equation eight atoms of manganese in the first member have 56 bonds, and a like amount in the second member has only 16, losing 40, and this 40 has been gained by the five atoms of arsenic. They now have 25, after gaining 40. They must then have had  $-15$  in the first place ( $25-40 = -15$ ). That is, the atom of arsenic in arsenious hydride has  $-3$  bonds ( $\text{As}^{'''}\text{H}_3$ ).



This equation illustrates the principle that free elements have no bonds. The tin gains two bonds, and these two bonds are taken from the mercury in the  $\text{HgCl}_2$ . If then the mercury had only two bonds which it has given up to the tin, it now has no bonds left ( $2-2 = 0$ ). Unless one denies that mercury has two bonds in  $\text{HgCl}_2$ , he must admit that free mercury has no bonds ( $\text{Hg}^\circ$ ), or, if it has any bonds, their algebraic sum is zero. We will not multiply examples, but ask that one reasoning upon this subject settle upon, (1st) a reasonable definition of the word bond; (2d) a reasonable definition of oxidation; (3d) that he does not overrule the conclusions to be reached by the simplest mathematics; (4th) that he consider carefully the principle here asserted, that no annihilation of bonds can take place.

Further the negative bond theory does not contradict the conclusions reached in the determination of structural formula, but the word bond is used in a totally different sense. Our bonds are oxidation bonds, not structural bonds. (See also next paragraph by Prof. Prescott.)

**Oxidation Valence** means degree of oxidation; and bonds are the units used in counting valence. Oxidation Valence should never be used to mean capacity for oxidation, but to denote actual, completed oxidation.

O. C. J.

**614.** As the term is ordinarily used by chemists, valence is a numerical measure of the *extent* of chemism, counted in the number of univalent atoms held in combination. Chlorine has one unit of valence in  $\text{HCl}$ ; oxygen has two units of valence in  $\text{H}_2\text{O}$ ; nitrogen has three units of valence in  $\text{H}_3\text{N}$ ; carbon has four units of valence in  $\text{H}_4\text{C}$ . The atom of hydrogen is a standard for the unit in valence, as it is for units of atomic and molecular weights. Leaving out of view the attempt to fix upon a constant valence, to be for any element always the same in every combination it can make, valence is here defined as the measure of the existing chemical union of any element, a measure found in a given compound or in a given set of compounds, or a series of measures found in different sets of compounds. Chlorine has a valence of one unit in chlorides because in these an atom of chlorine is found to hold one monad atom; it has a valence of five units in chlorates because in these each atom of chlorine is found to hold as many bonds as would satisfy five monad atoms. Other valences of chlorine are



found in other combinations of less frequent occurrence.\* In its usual sense, then, the valence of an element is the number of univalent atoms held in union by one atom of the element in question. The bond is the unit of valence. A bond is that extent of chemism which holds one monad atom in chemical union.

It is nearly ten years since Professor Johnson introduced† the use of positive and negative bonds in the chemical notation of oxidation and reduction. In this notation the bonds of every element are positive or negative or zero, according to whether the element be united with a negative body or a positive body or be uncombined, and as shown by rules (615).

The undersigned has elsewhere said‡ that chemism must be considered "a union or capacity of union of opposites, a union by the positive action of one atom with the negative action of another atom." In chemical union, then, there is a certain chemical polarity to the exercise of valence. The terms positive and negative may be adopted for the respective opposites in chemical union, with some correspondence to the polarity of electrical action. This polarity in chemism is well known to be for the most part merely relative. Sulphur is chemico-negative to hydrogen, but is positive to oxygen.

Accepting Prof. Johnson's original use of plus and minus signs for positive and negative bonds in notation, under his most delightful method of balancing equations for changes of oxidation, the writer has been led to go a step further,§ as follows: The valence of an atom in a given compound may be all positive or all negative, or partly positive and partly negative, this polarity being wholly relative in its nature. As nitrogen is negative to hydrogen, but positive to chlorine, therefore in ammonium chloride the atom of nitrogen has four negative bonds and one positive bond, thus:  $\text{N}^{-4} + ^1\text{H} + ^1\text{Cl} - 1$ , or  $\text{H} + ^1(-^4\text{N} + ^1)\text{Cl} - 1$ . Holding five monad atoms, the atom of nitrogen has five units of valence, or five bonds. Of these five units of valence, four are negative units and one is a positive unit, so that the algebraic sum of these units is negative three:  $\text{N}^{-4} + ^1 = \text{N}^{-3}$ . And in taking the valence measure, for balance of the results of oxidation and reduction, the nitrogen of ammonium chloride is found to have three negative bonds under the rule of Prof. Johnson. "In the notation of Prof. Johnson it is only the algebraic *sum* of the positive and the negative units of valence of any element or atom that is taken account of. This algebraic

\* It is said sometimes that valence ought to be, like atomic weight, a fixed attribute of any element, the same in all its combinations. Well, we do not find it to be so, and so far therefore it ought not to be so. Because the atomic weight of an element is the same in all its combinations, it does not follow that valence is always the same. It is certain that the strength of the chemism of any element is not the same in its unions with different elements, though it was at one time assumed that it must be the same.

† O. C. JOHNSON, 1880: *Chem. News*, **42**, 51.

‡ "Positive and Negative Units of Valence," A. B. PRESCOTT, 1887: *Proc. Am. Assoc. Advanc. Sci.*, **36**, 130.

§ *Proc. Am. Assoc. Advanc. Sci.*, **36**, 130.

sum of the positive and negative units should not be mistaken for the entire number of different units of valence, the latter number being all required in constitutional formulæ." Thus, to say that in ammonium chloride nitrogen has three negative bonds, no more, is to violate the first definition of a bond, "that extent of chemism which holds one monad atom in chemical union," for, certainly, five monad atoms are held here in combination.

On the other hand, to say that nitrogen in ammonia has three bonds, and that in nitric acid it has two more or just five bonds, is to make a very misleading statement, one that receives correction through Johnson's notation. In the conversion of ammonia into nitric acid by any oxidizing agent, not two but eight units of valence of the agent are consumed. As Prof. Johnson would say, the difference between minus 3 and plus 5 is a difference of 8 bonds, a statement that justifies the results of every-day operations in oxidation and reduction.

To affirm both the structural valence of modern chemistry and the oxidation valence of Prof. Johnson the following definitions are here offered: (1) VALENCE, counted in the number of its units, is a measure of the number of monad atoms held in chemical union. (2) Valence, counted in the algebraic sum of its positive and negative units, is the measure of the degree of oxidation. (3) A bond is a unit of valence, positive or negative, according to relations. In the measure of the number of monad atoms in union the arithmetic sum of the bonds is to be taken; in the measure of the degree of oxidation the algebraic sum of the bonds is to be taken. (4) Oxidation is an increase, and reduction is a decrease, in the algebraic sum of the units of valence.

An illustration of these definitions—which are presented merely in brief statement of what is well known—may be taken as follows. In dichloromethane,  $\text{C}^{+2-2}\text{H} + 1_2\text{Cl} - 1_2$ , the atom of the carbon has four bonds, that is, it holds four monad atoms in chemical union. Its degree of oxidation is zero, that is, two of its bonds are positive toward the chlorine and two are negative toward the hydrogen, so that its polarities are evenly balanced. (It is better not to say that it has no bonds.) The arithmetic sum of its units of valence is four; the algebraic sum of the same is zero. If the compound be oxidized to  $\text{CHCl}_3$ , the algebraic sum of the bonds of the carbon atom becomes plus two ( $\text{C}^{-1+3}=2$ ). If the compound be reduced to  $\text{CH}_3\text{Cl}$ , the algebraic sum of the bonds of the carbon atom becomes minus two ( $\text{C}^{-3+1}=-2$ ). But in  $\text{CH}_4$ , in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CH}_3\text{Cl}$ , alike, the carbon atom has four bonds—a valence denoting merely that it holds four atoms in chemical union.

The undersigned is compelled to go one step further, in his conception of the polarity of the units of valence, a step to reach some understanding of the union of the atoms of an element with each other. Such a union we

have between the two atoms of iron in a molecule of ferric chloride,\* thus  $\text{Cl} - 1, \text{Fe} + 4 \text{Fe} - 1 + 3 \text{Cl} - 1$ . The relation of the one atom of iron to the other is expressed thus,  $\text{Fe} + - \text{Fe}$ . Within the eight bonds of the two tetrads, there is one negative bond, so that the algebraic sum of all is plus six. As elsewhere stated, in presenting a hypothesis seemingly consistent with all facts, like atoms must be united to each other by valence positive in the one atom and negative in the other, as in elemental molecules and in the union of carbon to carbon in organic compounds. A. B. P.

### RULE FOR BALANCING EQUATIONS.

**615.** The number of oxidation bonds which any element has is determined by the following rules :

- Hydrogen has always one positive bond.
- Oxygen has always two negative bonds.
- Free elements either have no bonds, or the mathematical sum of those bonds is zero.

*d.* The sum of the bonds of any compound is zero.

*e.* In salts the bond of the metal is always positive.

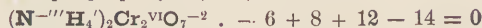
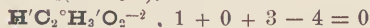
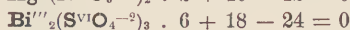
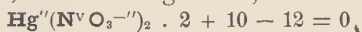
*f.* In acids and in salts the acid radical has only negative bonds.

Thus, the bond of free **Pb** is zero, but in **PbCl<sub>2</sub>** the lead has two positive bonds, and each atom of chlorine has one negative bond.

In **Bi<sub>2</sub>S<sub>3</sub>**, each atom of **Bi** has three positive bonds (*e*), and each atom of **S** has two negative bonds (*f*).

In ammonium nitrite **NH<sub>4</sub>NO<sub>2</sub>**, the **N** of the **NH<sub>4</sub>** has three negative bonds, each atom of **H** has one positive bond. The other **N**, that of the acid radical, **NO<sub>2</sub>**, has three positive bonds, and each atom of **O** has two negative bonds, the sum being zero  $-3 + 4 + 3 - 4 = 0$ .

In the following salts, etc., the bond of each element is marked above, with its proper sign, plus being understood if no sign is given. Then follows the equation in full, the bonds of each atom being multiplied by the number of atoms, and all being added, the sum is seen to be zero.



If the above is understood, the rule for balancing equations is easily explained.

THE NUMBER OF BONDS CHANGED IN ONE MOLECULE OF EACH SHOWS

\* See page 12, foot-note.

THE NUMBER OF THE MOLECULES OF THE OTHER WHICH MUST BE TAKEN, the words *each* and *other* referring to the oxidizing and reducing agents.

A few equations will illustrate the application of the rule.

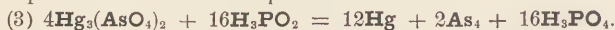


The **S** in the first member has 2 negative bonds (*a* and *d*); in the second member it has 6 positive, gaining 8 bonds; hence 8 molecules of **HNO<sub>3</sub>** must be taken. The nitrogen in the first member has five bonds, and in the second it has two. The difference is three, therefore just three molecules of **H<sub>2</sub>S** must be taken.



In this case, both the **Sb** and the **S** in the molecule gain bonds, and must be considered. It is plain (from *d* and *e*) that each atom of **Sb** gains 2 bonds, and the two in the molecule will gain 4.

The **S** in **Sb<sub>2</sub>S<sub>3</sub>** has 2 negative bonds, and in the second member (in **H<sub>2</sub>SO<sub>4</sub>**) it has 6 positive bonds—a gain of 8. The three atoms in the molecule will gain three times eight, or 24 bonds; to this add the 4 which the **Sb** has gained, and we have 28 bonds gained by one molecule of **Sb<sub>2</sub>S<sub>3</sub>**; hence 28 molecules of **HNO<sub>3</sub>** must be taken. We take 3 of **Sb<sub>2</sub>S<sub>3</sub>** for reasons explained in the first equation.



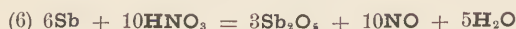
One atom of **Hg** loses 2 and three lose 6 bonds. One atom of **As** loses 5 and two will lose 10 bonds. The **Hg** and **As** together lose 16; hence take 16 of **H<sub>3</sub>PO<sub>2</sub>**. The **P** of **H<sub>3</sub>PO<sub>2</sub>** (hypophosphorous acid) has one bond, and in **H<sub>3</sub>PO<sub>4</sub>** it has 5—a gain of 4; hence 4 of **Hg<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>** must be taken.



The rule here requires 3 of **Cu** and 2 of **HNO<sub>3</sub>**, and in fact this is all that is used for oxidation, only two molecules of **NO** being formed; but 6 more of **HNO<sub>3</sub>**, which are not to be reduced, are required to unite with the **Cu**, making 8 in all.



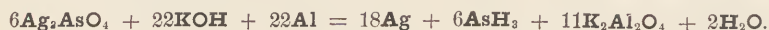
The **Hg** and the **I** together in one molecule of **Hg<sub>2</sub>I<sub>2</sub>** gain 14 bonds; but 12 more of undecomposed **HNO<sub>3</sub>** are required to unite with the **Hg**, or 26 in all.



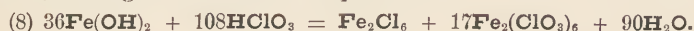
The rule calls for 3 of **Sb** and 5 of **HNO<sub>3</sub>**; but since the product **Sb<sub>2</sub>O<sub>3</sub>** cannot be written with an odd number of atoms, we must double the number of each and take 6 and 10 instead of 3 and 5.



The **Pb** and the **N** lose 18 bonds, and the **Al** gains 3; but since 3:18::1:6, we take the latter ratio because the numbers are smaller.

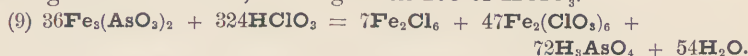


Here the rule calls for 3 of **Ag<sub>2</sub>AsO<sub>4</sub>**, and 11 of **Al**; but we double these numbers, taking 6 and 22, as in equation 6.

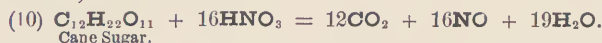




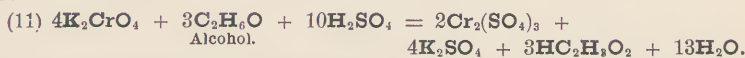
That portion of the **Cl** which is reduced loses 6 bonds and the **Fe** gains one, so the ratio would be 6 and 1 ; but **Fe<sub>2</sub>Cl<sub>6</sub>** cannot be written with one of **Cl**, so instead of taking 6 and 1, we take 36 of **Fe(OH)<sub>2</sub>** and 6 of **HClO<sub>3</sub>**. Now, one of **Fe<sub>2</sub>Cl<sub>6</sub>** is formed, and the rest of the **Fe** becomes **Fe<sub>2</sub>(ClO<sub>3</sub>)<sub>6</sub>**. But 102 molecules of unredueed **HClO<sub>3</sub>** will be required to unite with the remaining 34 atoms of **Fe**, making in all 108 of **HClO<sub>3</sub>**.



The **Cl** loses 6 and the ferrous arsenite gains 7 bonds ; but since **Fe<sub>2</sub>Cl<sub>6</sub>** cannot be written with 7 atoms of **Cl**, we must take larger numbers, having the ratio of 6 to 7. It will be seen that 36 of **Fe<sub>3</sub>(AsO<sub>3</sub>)<sub>2</sub>** and 42 of **HClO<sub>3</sub>** are the smallest numbers that will answer. This gives us 7 of **Fe<sub>2</sub>Cl<sub>6</sub>**, but enough unredueed **HClO<sub>3</sub>** must be taken to unite with the remaining 94 atoms of **Fe** ; for this purpose 282 will be required, which, with 42 which are reduced, makes 324.



This takes place with **HNO<sub>3</sub>**, specific gravity 1.50. The sum of the bonds of the **C** in the first member is equal to zero, in the second member these 12 atoms have 48 bonds ; hence take 3 and 48, or simpler, 1 and 16.



The two atoms of **C** in the alcohol have 4 negative bonds, and in the acetic acid their bonds are equal to zero, gaining 4 bonds ; hence take 4 of **K<sub>2</sub>CrO<sub>4</sub>**. The **Cr** loses 3, so we take 3 of alcohol and 10 of **H<sub>2</sub>SO<sub>4</sub>**, enough to combine with the **K** and the **Cr**.



Unless **HNO<sub>3</sub>** of proper strength and temperature be employed, other products are formed, and, if the **HNO<sub>3</sub>** is strong enough, nitroglycerine.

The 3 atoms of **C** in the glycerine have two negative bonds, but in the second member the same 3 atoms have 12 positive bonds, gaining 14 ; hence we take 14 molecules of nitric acid and because the nitrogen loses three bonds we take three molecules of the glycerine.

**THE NON-METALLIC ELEMENTS** will be described in the order of their atomic weights. And the acids in the order of oxidation valence ; the acid in which the element has the lower number of bonds being placed first.

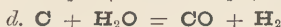
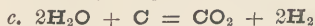
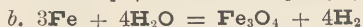
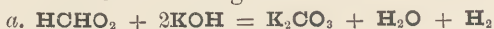
## HYDROGEN. $\text{H} = 1.$

**616.** *Specific gravity*, 0.069234. A **crith** is the weight of one litre of hydrogen. It is taken as the *unit* of weight for gases. Thus one litre of

oxygen weighs 15.9633 criths, and one litre of bromine weighs 79.768 criths. At 0° C. one crith (one litre) of hydrogen weighs 0.089578 grammes, the barometer showing 760 mm. (about 30 inches) pressure. Its vapor density (1.00) shows that its molecule has two atoms,  $H_2$ .

**617. Occurrence.**—It is rarely found in nature in a free state. Volcanic gases, and gases from oil wells, sometimes contain hydrogen in a free state. It has been found occluded in meteorites, and by means of the spectroscope it is found in the atmosphere of the sun.

**618. Production.**—Hydrogen is produced : (1) By electrolysis of water. (2) By the action of potassium or sodium amalgam upon water. (3) By the action of certain dilute acids upon the easily oxidized metals. Details are specified in the description of each acid. (4) By dissolving zinc or aluminium in solutions of fixed alkalis ; better in presence of finely divided iron or platinum. (5) By action of heat upon formic or oxalic acid in presence of a fixed alkali hydroxide (*a*). (6) By action of steam upon red hot metals, such as iron (*b*). (7) By action of steam upon red hot carbon (charcoal, coke, or anthracite coal) (*c*). Methods 5 and 6 are used in the production of the so-called “water gas.”



Reaction (*c*) takes place at a red heat. The  $CO_2$  may be separated by passing the mixed gases through lime-water. Reaction (*d*) takes place at a white heat.

**619. Properties.**—A colorless and odorless gas ; not poisonous, but causes death by exclusion of air. It is the lightest body known. Hence it is the best gas for filling balloons, but illuminating gas is sometimes used, being cheaper. Sound travels three times faster in it than in air. It refracts light more powerfully than any other gas, and six times as much as air. Under a pressure of 650 atmospheres at -140° C. (-220° F.) it condenses to a liquid. This extreme cold is obtained by the rapid evaporation of liquid  $SO_2$  and  $CO_2$ . Many metals absorb hydrogen slightly. Palladium most of all. According to GRAHAM, palladium wire at a red heat absorbs 935, and at ordinary temperatures, 375 times its volume of hydrogen.

In this occluded condition it reduces  $Fe_2Cl_6$  to  $FeCl_2$ , and  $HgCl_2$  to metallic mercury. Hydrogen burns with a non-luminous, very hot flame, giving more heat than an equal weight of any other element, or any mixture of elements. One gramme in burning produces heat enough to raise 34462 grammes of water from 0° to 1° C. A like amount of charcoal carbon, when burned to  $CO_2$ , only produces heat enough to raise 8080 grammes of water one degree C. (FAVRE and SILBERMANN).

Hydrogen is usually estimated by measure rather than by weight.

**620. Oxidation.**—Chlorine and bromine unite directly with hydrogen

in the sunlight, but heat is required to effect its combination with iodine, fluorine, and oxygen.

All oxides, hydroxides, nitrates, carbonates, oxalates, and organic salts of the following elements are reduced to the metallic or elemental state by ignition in hydrogen gas: **Pb, Ag, Hg, Sn, Sb, As, Bi, Cu, Cd, Pd, Mo, Ru, Os, Rh, Ir, Te, Se, W, Fe, Co, Ni, Zn, Tl, Nb, In, V.**

Compounds of aluminium, manganese, and of the fourth and fifth group metals have not been reduced by hydrogen.

### BORON. $B = 10.941$ .

**621. Specific gravity** (crystallized), 2.615 (HAMPE, 1876). Infusible at ordinary white heat, melts in the electric arc. **Occurrence.**—Not found free in nature. Occurs chiefly as borax,  $\text{Na}_2\text{B}_2\text{O}_7$ , and boracic acid,  $\text{H}_3\text{BO}_3$ , in volcanic districts.

**Preparation.**—(1) By electrolysis. (2) By fusion of  $\text{B}_2\text{O}_3$  with **Na**. (3) By fusing  $\text{B}_2\text{O}_3$  with **Al**, and then dissolving the **Al** by  $\text{Na}(\text{OH})$ . (4) By igniting  $\text{BCl}_3$  with hydrogen. (5) By fusing dry borax with amorphous phosphorus. (6) By fusing  $\text{NaBF}_4$ ,  $\text{KBF}_4$ , or  $\text{B}_2\text{O}_3$  with **Mg**.

**622. Properties.**—There are two varieties of boron, the amorphous and the crystalline. The former is changed to the latter by heating to  $1600^\circ \text{C}$ . for two hours in presence of aluminium and carbon. Amorphous boron is a greenish-brown opaque powder; odorless, tasteless, a non-conductor of electricity, insoluble in water, alcohol, and ether. Heated in oxygen burns to  $\text{B}_2\text{O}_3$ ; heated in air burns to  $\text{B}_2\text{O}_3$  and **BN**. Combines on heating, directly with **S, Cl, Br, N**, etc. It dissolves in sulphuric and nitric acids, forming  $\text{H}_3\text{BO}_3$ ; in chlorine forming  $\text{BCl}_3$ . It is oxidized by heating in **KOH**, forming  $\text{K}_2\text{BO}_3$  and **H**; and by heating in alkaline carbonates, producing free carbon. Many metallic chlorides and sulphides—*e.g.*,  $\text{PbCl}_2$ ,  $\text{AgCl}_2$ ,  $\text{PbS}$ —are reduced to the metallic state when heated with boron.

### BORIC ACID. $\text{H}_3\text{BO}_3$ .

**623. Oxidation valence**..... $\text{H}'_3\text{B}'''\text{O}''_3$



**Structural valence**..... $\text{H}-\text{O}-\text{B}-\text{O}-\text{H}$

Three kinds of boric acid are known: **Orthoboric**,  $\text{H}_3\text{BO}_3$ , formed by dissolving  $\text{B}_2\text{O}_3$  in water; heated to  $100^\circ \text{C}$ . it forms **metaboric acid**,  $\text{H}_2\text{B}_2\text{O}_4$ ; heated for a long time at  $160^\circ \text{C}$ . **pyroboric acid**,  $\text{H}_2\text{B}_4\text{O}_7$ , is formed; heated to about  $300^\circ \text{C}$ .,  $\text{B}_2\text{O}_3$  remains.

**624.** The **Borates** of the metals of the alkalis are **soluble in water**; those of the other metals are insoluble in water, but in general are made soluble by free boric acid. They are all nearly or quite insoluble in alcohol. Borates are identified especially by the green color they impart to flames.

**625.** **Silver nitrate** forms, in solutions of acid borates, a white precipitate of *silver borate*,  $\text{Ag}_2\text{B}_2\text{O}_4$ , but normal borates form in part silver oxide, brown. **Lead acetate** gives a white precipitate of *lead borate*,  $\text{Pb}(\text{BO}_2)_2$ ; **calcium chloride**, in solutions not very dilute, a white precipitate of *calcium borate*; and **barium chloride**, in solutions not dilute, a white precipitate of *barium borate*,  $\text{Ba}(\text{BO}_2)_2$ . With **aluminium salts**, the precipitate is *aluminium hydroxide*.

**626.** Borates are transposed with formation of boracic acid, by all ordinary acids—in some conditions even by carbonic acid; the transposition being partial when soluble products result, as with phosphoric acid.

The liberated boracic acid is dissolved by **alcohol**, and if the alcohol solution be set on fire, it burns with a *green flame*.

**627.** A solution of a borate, acidulated with hydrochloric acid to a barely perceptible acid reaction, imparts to a slip of **turmeric paper** half wet with it, a dark-red color, which on drying intensifies to a characteristic *red color*.

By heating a mixture of borax, acid sulphate of potassium, and a fluoride, fused to a bead on the loop of platinum wire, in the clear flame of the Bunsen gas-lamp, an evanescent yellowish-green color is imparted to the flame.

Borates fused in the *inner blow-pipe flame* with potassium acid sulphate give the *green color* to the outer flame.

If a crystal of boric acid, or a solid residue of borate previously treated with sulphuric acid, on a porcelain surface, is played upon by the flame of Bunsen's Burner, the green flame of boron is obtained.

**628.** If a powdered borate (previously calcined), is moistened with sulphuric acid and heated on platinum wire to expel the acid, then moistened with **glycerine** and burned, the green flame appears with great distinctness.

The glycerine is only ignited, then allowed to burn by itself. Barium does not interfere (being held as sulphate, non-volatile); copper should be previously removed in the wet way. The glycerine flame gives the spectrum. But in all flame tests, boric acid must be liberated.

Borates (fused on platinum wire with sodium carbonate) give a characteristic spectrum of four lines, equidistant from each other, and extending from **Ba**  $\gamma$  in the green to **Sr**  $\delta$  in the blue.

Boric acid is **estimated**: (1) As  $\text{KBF}_4$ . (2) By adding a known quan-



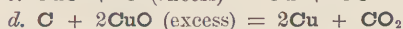
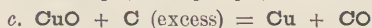
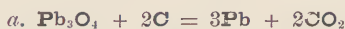
tity of  $\text{Na}_2\text{CO}_3$ , fusing and weighing; then after determining the  $\text{CO}_2$  subtracting its weight and that of the  $\text{Na}_2\text{O}$  present (calculated from  $\text{Na}_2\text{CO}_3$  first added). The difference is the weight of  $\text{B}_2\text{O}_3$  present.

### CARBON. C = 11.9736.

**629. Specific gravity**, diamond, 3.518 (BAUMHAUER, 1887); graphite, 2.32 (RAMMELSBURG, 1873); hard gas coke, 2.356 (MARCHAND and MEYER); charcoal, 1.45 to 1.7 (VIOLETTE, 1853).

**630. Occurrence.**—Diamond is the only form of carbon that cannot be artificially prepared. It is the hardest substance known. It burns at a white heat to  $\text{CO}_2$  in oxygen gas, and in air. Graphite occurs native, both crystalline and amorphous. It is a hard, gray, metal-like, opaque solid. When pig-iron is dissolved in acids, graphite remains. At a white, but not at a red heat, graphite very slowly burns to  $\text{CO}_2$ . It is slowly oxidized when heated with  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$ . Graphite is used in lead-pencils; in black-lead (plumbago) crucibles; as a lubricator; in battery plates; for the carbon of arc-lights, etc. Boiled with  $\text{KClO}_3$  and  $\text{HNO}_3$  graphitic acid,  $\text{C}_{11}\text{H}_4\text{O}_8$  (?) is produced, which after drying burns almost explosively. Charcoal is made by heating wood in closed iron retorts. Lamp-black is made by burning vegetable matters, rich in carbon, such as resin, tar, wax, fat, coal-gas, etc., in a limited supply of air. Used as a pigment, and in stove-blackening, printer's ink, etc. Ordinary charcoal (better animal charcoal) is used in water-filters. Charcoal absorbs very many gases. According to SAUSSURE, one volume of beech-wood charcoal at  $12^\circ \text{C}$ . and 724 mm. pressure, absorbs 9.42 volumes of  $\text{CO}$ , 35 of  $\text{CO}_2$ , 55 of  $\text{H}_2\text{S}$ , 65 of  $\text{SO}_2$ , 85 of  $\text{HCl}$ , and 90 of  $\text{NH}_3$ .

**631. Oxidation.**—Carbon is oxidized to  $\text{CO}_2$  by fusing with  $\text{KNO}_3$  or  $\text{KClO}_3$ . By igniting in  $\text{CO}_2$ , the whole of the carbon is changed to  $\text{CO}$  ( $\text{CO}_2 + \text{C} = 2\text{CO}$ ). The free carbon gaining two bonds of oxidation valence, and the carbon of the  $\text{CO}_2$  losing two bonds. By simple ignition with carbon, all oxides of the elements in the following list are reduced to the elemental state; and if sodium carbonate is added, all of the salts of the same are likewise reduced. Cu, Bi, Cd, Pb, Ag, Hg, As, Sb, Sn, Pd, Mo, Ru, Os, Rh, Ir, Te, Se, W, K, Na, Rb, Cr, Fe, Mn, Co, Ni, Zn, Ti, Tl.



With excess of carbon  $\text{CO}$  is formed (c). With excess of the oxide  $\text{CO}_2$  is formed (d). In the reduction of iron ore, the process is conducted so as to

give some  $\text{CO}$  and some  $\text{CO}_2$ . To obtain some metals in the free state (such as **K** and **Na**), special methods are adopted to exclude the air, and to produce the high temperature needed.

### ACETIC ACID. $\text{HC}_2\text{H}_3\text{O}_2$ .

632. Oxidation valence..... $\text{H}'\text{C}^\circ_2\text{H}'_3\text{O}''_2$

Structural valence..... $\text{H}-\underset{\text{H}}{\overset{\text{H O}}{\underset{|}{\text{C}}}}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{O}-\text{H} = \text{CH}_3.\text{CO}_2\text{H}$

Absolute acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , is a transparent solid. *Specific gravity*, 1.0607 (MENDELÉEFF, 1860). Its observed vapor density, 29.7, shows its molecule to be  $\text{HC}_2\text{H}_3\text{O}_2$  and not  $\text{H}_2\text{CO}$ . Found in small quantities in the juices of some plants.

**Production.**—(1) By dry distillation of wood. (2) By action of atmospheric oxygen, chromic acid, nitric acid, hypochlorous acid, and other oxidizing agents upon alcohols, especially under the influence of ferments. (3) By action of **KOH** or **NaOH** at high temperatures upon various organic bodies—*e.g.*, tartaric, citric, and malic acids, sugar, alcohol, etc. The absolute acid melts at about  $16^\circ \text{C}$ . and boils at  $119^\circ \text{C}$ .

It vaporizes gradually from its water solutions at ordinary temperatures; more rapidly as they are stronger, the vapor having the characteristic odor of vinegar.

633. The salts of acetic acid—the metallic **Acetates**—are all soluble in water; *argentic and mercurous acetates but sparingly soluble*. Most of the acetates, except mercurous and silver acetates, dissolve in alcohol. They have a slight odor of the acid. For **identification**, the odor of the acid, and of its ether (636), and the color of the ferric solution (635), are employed. Ignition-tests, 638.

634. The stronger mineral acids transpose acetates, forming acetic acid. Solid acetates, with concentrated sulphuric acid, evolve strong acetous vapor; but if the heat be somewhat increased, the mixture blackens from separation of carbon, and at higher temperatures sulphurous and carbonic anhydrides are evolved.

635. Solution of **ferric chloride** forms, with solutions of acetates, a *red solution* containing *ferric acetate*,  $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_6$ , which on boiling precipitates brownish-red, basic ferric acetate. The red solution is not decolorized by solution of mercuric chloride (distinction from thiocyanate); but is decolorized by strong acidulation with sulphuric acid or hydrochloric acid (distinction from thiocyanate and from meconate). The ferric acetate is precipitated by alkali hydroxides.

636. If acetic acid or an acetate be warmed with **sulphuric acid** and a

*little alcohol*, the characteristic pungent and *fragrant odor of ethyl acetate* or acetic ether is obtained :



**637.** Acetic acid does not act as a **Reducing Agent** as readily as do most of the organic carbon compounds. It reduces permanganates and chromates but slowly, even in boiling solution ; reduces auric chloride only in alkaline solution, and does not reduce alkaline copper solution. It takes chlorine into combination—slowly in ordinary light, quickly in sunlight, forming chloracetic acids.

**638.** By **ignition** alone, acetates blacken, with evolution of vapor of *acetone*,  $\text{C}_3\text{H}_6\text{O}$ , inflammable and of an agreeable odor. By prolonged ignition of acetates in the air, carbonates are obtained free from charcoal.—By ignition with **alkali hydroxides** in dry mixture, *marsh-gas*,  $\text{CH}_4$ , is evolved.—By ignition with **alkalies** and **arsenious anhydride**, the offensive vapor of cacodyl-oxide is obtained (473).

#### CITRIC ACID. $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ .

Oxidation valence of its elements. . . .  $\text{H}'_3\text{C}'_6\text{H}'_5\text{O}''_7$   
 $\text{CHHCO}_2\text{H}$

Structural valence of its elements. . . .  $\text{C}(\text{OH})\text{CO}_2\text{H}$   
 $\text{CHHCO}_2\text{H}$

**639.** Found in small quantities in the juices of many fruits. The chief commercial source is lemon-juice. It is a colorless, crystallizable, non-volatile solid ; freely soluble in water and in alcohol.

The **Citrates** of the metals of the alkalies are freely **soluble in water** ; those of iron and copper are moderately soluble ; those of the alkaline earth metals insoluble. There are many soluble double citrates formed by action of alkali citrates upon precipitated citrates, or of alkali hydroxides upon metallic salts in presence of citric acid. In **distinction** from tartrates, the solubility of the potassium salts (642) ; non-precipitation of calcium salt in cold solution ; and weaker reducing action, are to be noted.

**640.** Solution of **calcium hydroxide** in excess (as by dropping the solution tested into the reagent) gives no precipitate with citric acid or citrates in the cold (distinction from tartaric acid), but on heating, the white *calcium citrate*,  $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ , is precipitated (not soluble in cold potassium hydroxide solution). By filtering before boiling, the tartrate and citrate may be approximately separated. Calcium chloride also gives the same precipitate after boiling. Calcium citrate is soluble in acetic acid (distinction from oxalates).

**641.** Solution of **lead acetate** precipitates white, *lead citrate*,  $\text{Pb}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ , soluble in ammonia. **Silver nitrate** gives a white precipitate of *silver citrate*,  $\text{Ag}_3(\text{C}_6\text{H}_5\text{O}_7)$ , which does not blacken on boiling (distinction from tartrate).

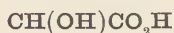
**642.** One part of citric acid dissolved in two parts of water, and treated with a solution of one part of potassium acetate in two parts of water, should remain clear *after* addition of an equal volume of strong alcohol (absence of oxalic acid and of tartaric acid and its isomers).

**643.** Citric acid does not act very readily as a **reducing agent** ; does not reduce alka-

line copper solution, or silver solution, or permanganate but very slowly. Concentrated nitric acid produces from it, acetic and oxalic acids; and digestion with manganese dioxide decomposes it, with formation of acetone, acrylic, and acetic acids. Citrates carbonize on **ignition**, with various empyreumatic products, and with final formation of carbonates. By fused potassium hydroxide, short of ignition, they are decomposed with production of oxalate and acetate.

### TARTARIC ACID. $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ .

Oxidation valence of its elements...  $\text{H}'_2(\text{C}_4)^{\text{VI}}\text{H}'_4\text{O}''_6$



Structural valence of its elements... I



**644.** Tartaric acid is found in various fruits. The chief commercial source is grape-juice.

Tartaric acid is a colorless, crystallizable, non-volatile solid, freely soluble in water, and in alcohol. It may be separated from bases by adding sulphuric acid and alcohol.

The **Tartrates** of the alkali bases are **soluble in water**; the normal tartrates being freely soluble, the acid tartrates of potassium and ammonium sparingly soluble. The tartrates of the alkaline earth bases and of the non-alkali bases, are insoluble or sparingly soluble, but mostly dissolve in solution of tartaric acid. Most of the tartrates are insoluble in alcohol. There are double tartrates of heavy metals with alkali metals, which dissolve in water.

Hydrochloric, nitric, and sulphuric **acids** transpose the tartrates (whether forming solutions or not). Most of the tartrates are also dissolved (and, if already dissolved, are not precipitated) by the **alkali hydroxides**, owing to the formation of soluble double tartrates (153).

The potassium acid tartrate, precipitated with help of alcohol, and the silver reduction, are of greatest **analytical** interest.

**645.** Solution of **calcium hydrate**, added to alkaline reaction, precipitates from cold solution of tartaric acid, or of soluble tartrates, *calcium tartrate*, white,  $\text{Ca}(\text{C}_4\text{H}_4\text{O}_6)$ . Solution of calcium chloride with neutral tartrates, gives the same precipitate. Solution of calcium sulphate forms a precipitate but slowly, or not at all (distinction from racemic acid). The precipitate of calcium tartrate is soluble in cold solution of potassium hydroxide, precipitated gelatinous on boiling, and again made soluble on cooling (distinctions from citrate), and dissolves in acetic acid (distinction from oxalate).

**646.** **Silver nitrate** precipitates, from solutions of normal tartrates, *silver tartrate*,  $\text{Ag}_2(\text{C}_4\text{H}_4\text{O}_6)$ , white, becoming black when boiled. If the precipitate is filtered, washed, dissolved from the filter by dilute ammonium hydroxide into a clean test-tube, left for a quarter of an hour on the water-



bath, the silver is reduced as a *mirror coating* on the glass (421), distinction from citric acid. Free tartaric acid does not reduce silver salts. **Permanganate** is reduced quickly by alkaline solution of tartrates (distinction from citrates), precipitating manganese dioxide, brown. Free tartaric acid acts but slowly on the permanganate. Alkaline copper tartrate resists reduction in boiling solution. **Chromates** are reduced by tartaric acid, the solution turning green. The oxidized products, both with permanganate and chromate, are formic acid, carbonic anhydride, and water.

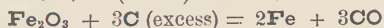
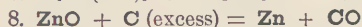
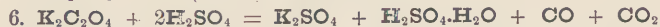
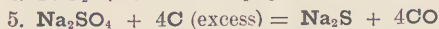
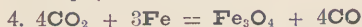
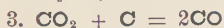
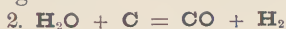
647. On ignition, tartaric acid or tartrates evolve the *odor of burnt sugar, separating carbon*, and becoming finally converted to carbonates.—Strong sulphuric acid also blackens tartrates, on warming. Melted potassium hydroxide, below ignition, produces acetate and oxalate.

### CARBON MONOXIDE. CO.

Oxidation valence of its elements.....C''O''

Vapor density, 14; fixing the molecular formula as CO, and not C<sub>2</sub>O<sub>2</sub>.

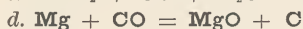
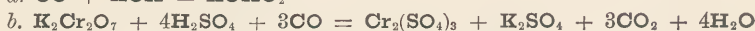
648. Preparation.—(1) By burning carbon in a limited supply of air. (2) By passing steam over excess of charcoal at a white heat. (3) By passing CO<sub>2</sub> over red hot charcoal. (4) By passing CO<sub>2</sub> over red hot Fe. (5) By heating Na<sub>2</sub>SO<sub>4</sub> with excess of charcoal. (6) By heating an oxalate or formate with concentrated H<sub>2</sub>SO<sub>4</sub>. (7) By heating together K<sub>4</sub>Fe(CN)<sub>6</sub> and concentrated H<sub>2</sub>SO<sub>4</sub>. If the H<sub>2</sub>SO<sub>4</sub> is dilute, HCN is formed. (8) By heating metallic oxides with an excess of charcoal.



649. Properties.—At ordinary pressure liquefies at -193° C. (WROBLEWSKI, 1884). Under pressure of not less than 50 atmospheres, liquefies at -136° C. (OLSZEWSKI, 1884). Pressure without cold has as yet failed to liquefy it. It is a narcotic poison. It burns in the air to CO<sub>2</sub>, explosively if mixed in suitable proportions. Does not support combustion. Combines with Cl in the sunlight, forming phosgene gas, COCl<sub>2</sub>. Forms potassium formate when warmed with KOH (a). It is oxidized to CO<sub>2</sub> by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and H<sub>2</sub>SO<sub>4</sub> (b), and by PdCl<sub>2</sub>, Pd being formed (c). Heated to a white heat with K or Na or Mg, free carbon is formed.

After separation from interfering gases, it is estimated: (1) By absorption by a "papier-maché" ball of Cu<sub>2</sub>Cl<sub>2</sub>. (2) It is absorbed by a similar

ball of **KOH** (see equation (a) below). These balls are placed in a measured portion of the gas, and the decrease in volume shows the amount of **CO** that has been absorbed. The reducing action upon oxides by charcoal mentioned in 631 may (theoretically) be produced by carbon monoxide, but conclusive experiments have not been reported upon all, and there may be exceptions.



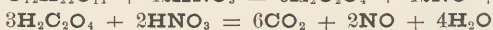
### OXALIC ACID. $\text{H}_2\text{C}_2\text{O}_4$ .

Oxidation valence of its elements. . .  $\text{H}'_2\text{C}'''\text{O}''_2$

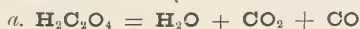
Structural valence of its elements. . .  $\text{H}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\text{H}$

**650. Occurrence.**—Found in many plants, either in a free state or as an oxalate. In sorrel it is found as  $\text{KHC}_2\text{O}_4$ ; in rhubarb as  $\text{CaC}_2\text{O}_4$ .

**Production**—(1) By action of nitric acid sp. gr. 1.38 upon sawdust, starch, or sugar. By the continued action of concentrated nitric acid, after the sugar is all oxidized to oxalic acid, the latter is farther oxidized to  $\text{CO}_2$ . (2) By heating sawdust with **KOH** or **NaOH**. Hydrogen is evolved, the cellulose,  $\text{C}_6\text{H}_{10}\text{O}_5$ , being converted into oxalic acid. Under certain conditions, additional products are formed. It is also formed in the oxidation of a great many organic compounds.



**651.** Absolute oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is a white, amorphous solid, which by care may be sublimed with only partial decomposition (a), at about  $165^\circ\text{C}$ . ( $329^\circ\text{F}$ .) *Crystallized oxalic acid*,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , effloresces very slowly in warm, dry air, and melts in its crystallization-water at  $98^\circ\text{C}$ . ( $208^\circ\text{F}$ .); at which temperature the liquid soon evaporates to the absolute acid. Oxalic anhydride is not formed.



**Concentrated sulphuric acid**, with a gentle heat, decomposes *oxalic acid*, by removing the elements of water from it, with effervescence of *carbon dioxide* and *carbon monoxide*, according to the equation in the preceding paragraph. With *oxalates*, the decomposition generates the same gases. Other strong dehydrating agents produce the same result.

The *effervescing gas*,  $\text{CO}_2 + \text{CO}$ , gives the reactions for carbonic anhydride; also, if in a sufficient quantity, it will *burn with a blue flame*, when ignited, by the oxidation of the carbon monoxide.

**652.** The **Oxalates** of the metals of the alkalies are **soluble in water**; nearly all those of the other metals are either insoluble or sparingly soluble in water. (Chromic oxalate is freely soluble in water; magnesian oxalate, sparingly soluble.)

In **analysis**, calcium oxalate is the precipitate most used, soluble in hydrochloric, not in acetic, acid. Also, the reducing action (655), decomposition with sulphuric acid (651), and ignition (656), serve in identification.

**653.** The metallic oxalates, soluble and insoluble, are transposed by **dilute sulphuric, hydrochloric, and nitric acids**, with formation of *oxalic acid*:



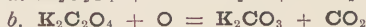
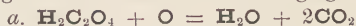
That is: the precipitated oxalates of those metals, which form soluble chlorides, *dissolve in dilute hydrochloric acid*; of those metals which form soluble sulphates, in dilute sulphuric acid; and all precipitated oxalates dissolve in dilute nitric acid.

**Acetic acid** does not dissolve precipitated oxalates, or but slightly. Certain of the oxalates dissolve, to some extent, in **oxalic acid** (as acid oxalates).

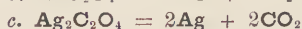
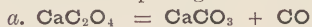
**654.** The *precipitates of oxalates are white*. It follows, from 653, that solution of *oxalic acid* can be precipitated but very slightly by any metallic salts of the stronger acids.

Solutions of metallic *oxalates* give, with soluble **salts of calcium**, a quite complete precipitate of *calcium oxalate*,  $\text{CaC}_2\text{O}_4$ ; with **salts of barium**, in solutions not very dilute, a slightly soluble precipitate of *barium oxalate*,  $\text{BaC}_2\text{O}_4$ ; with **ferrous salts**, a yellowish precipitate of *ferrous oxalate*,  $\text{FeC}_2\text{O}_4$ , not soluble in oxalic acid; with salts of **lead**, as stated in 394; with salts of **silver**, a characteristic reaction, as stated in 418 and 656 c.

**655.** Oxalic acid is a decided **Reducing Agent**, being converted to *water and carbonic anhydride (a)*, and the metallic oxalates to *carbonates and carbonic anhydride (b)*, by all strong oxidizing agents. The action of oxidizing agents is given in 659.



**656.** The oxalates are all dissociated on ignition. Those of the metals of the alkalies and alkaline earths are resolved at an incipient red heat, into carbonates and carbon monoxide (*a*)—a higher temperature decomposing the carbonates. The oxalates of metals, whose carbonates are easily decomposed, but whose oxides are stable, are resolved into oxides, carbonic anhydride, and carbon monoxide (*b*). The oxalates of metals, whose oxides are decomposed by heat, leave the metal, and give off carbonic anhydride (*c*). As an example of the latter class, *silver oxalate*, when heated before the blow-pipe, decomposes explosively, with a sudden puffing sound—a test for oxalates:



**657. a.** Oxalates are formed by treating the oxide, hydroxide, or carbonate with oxalic acid. In this manner may be made the oxalates of **Pb**,

Ag, Hg', Hg'', Sn'', Bi, Cu'', Cd, Zn, Al, Co'', Ni, Mn'', Fe'', (Fe<sub>2</sub>)<sup>VI</sup>, (Cr<sub>2</sub>)<sup>VI</sup>, Ba, Sr, Ca, Mg, Na, and K. And some others.

*b.* By adding oxalic acid to some soluble salt of the metal. In this manner the above oxalates may be made, except alkali, magnesium, chromic, ferric, aluminic, and stannic oxalates, which are not precipitated. Antimonious salts are precipitated, but the precipitate is basic.

*c.* Alkaline oxalates will precipitate the same solutions as oxalic acid, but many of the precipitates are soluble in excess of the alkaline oxalate, and, as a rule, the salt found is a double one, *e.g.*,  $\text{AgNH}_4\text{C}_2\text{O}_4$ . The fourth-group metals are well-defined exceptions to this rule—their precipitates, formed by this method, being normal oxalates.

*d.* Some of the metals when finally divided are attacked by oxalic acid, hydrogen being evolved.

**658. Estimation.**—(1) It is precipitated as  $\text{CaC}_2\text{O}_4$ ; after washing, the Ca is determined by (141), from which the oxalic acid is calculated. (2) By the amount of  $\text{K}_2\text{Mn}_2\text{O}_8$  which it will reduce. (3) By measuring the amount of  $\text{CO}_2$  evolved when it is oxidized in any convenient manner, usually by  $\text{MnO}_2$ . (4) By the amount of gold it reduces from  $\text{AuCl}_3$ .

**659. Oxidation.**—As a rule, reducing agents have no action on oxalic acid at ordinary temperatures. By fusion, however, a few metals, K, Na, Mg, etc., reduce it to free carbon.

$\text{HNO}_2$  *b.* Nitrous acid seems to have no action on oxalic.

$\text{HNO}_3$  *c.*  $\text{NO}$  is formed, and the oxalic becomes  $\text{CO}_2$  [*Gmelin's Hand-book*, 9, 116].

*Experiment:* To dry oxalic acid add nitric acid, sp. gr. 1.42, or, better, 1.50. Test the evolved gas for  $\text{CO}_2$  by passing it into a solution of barium chloride containing free potassium hydroxide.

$\text{Cl}$  *d.*  $\text{HCl}$  is formed, and the oxalic becomes  $\text{CO}_2$  [*Gmelin's Hand-book*, 9, 116]. This change of bonds takes place more readily in presence of potassium hydroxide, forming  $\text{KCl}$ .

$\text{HClO}$  *e.* Forms  $\text{CO}_2$  and  $\text{Cl}$  [*Watts' Dictionary of Chemistry*, 4, 250; *Wurtz's Dictionnaire de Chimie*, 2, 670]. If the oxalic acid is in excess,  $\text{HCl}$  is formed. The action is more rapid in presence of fixed alkali, an alkali chloride being formed.

$\text{HClO}_3$  *f.* Forms  $\text{CO}_2$  and varying proportions of  $\text{Cl}$  and  $\text{HCl}$ . A high degree of heat and excess of oxalic acid favoring the production of  $\text{HCl}$  [*Calvert and Davies, Jour. Chem. Society*, II. 193].

$\text{Br}$  *g.* Does not decompose oxalic acid, except in alkaline mixture, forming a bromide and a carbonate.

$\text{HBrO}_3$  *h.* Bromine and  $\text{CO}_2$  are formed.

$\text{HIO}_3$  *i.* Forms  $\text{CO}_2$  and  $\text{I}$  [*H. Davy*].



The following acids do not change the bonds of oxalic acid: Carbonic, phosphoric, hypophosphorous, hydrosulphuric, sulphuric (but see 651), hydrochloric, hydrobromic, hydriodic, hydrocyanic, thiocyanic, ferrieyanic, ferroeyanic.

**Pb''' k.**  $\text{PbO}_2$  with oxalic acid forms lead oxalate and  $\text{CO}_2$ .

Oxalic acid has no action upon  $\text{Pb}_3\text{O}_4$ , but reduces it quickly in presence of any acid capable of changing the  $\text{Pb}_3\text{O}_4$  to  $\text{PbO}_2$ .

**Hg'' l.** Oxalate of ammonia boiled in the sunlight gives  $\text{Hg}_2\text{Cl}_2$  and  $\text{CO}_2$  [*Gmelin's Hand-book*, 9, 118; *Watts' Dictionary of Chemistry*, 4, 251].

Free oxalic acid boiled in the sunlight also gives  $\text{Hg}_2\text{Cl}_2$ .

**As<sup>v</sup> m.**  $\text{H}_3\text{AsO}_4$  becomes  $\text{H}_3\text{AsO}_3$ , and  $\text{CO}_2$  is evolved.

To prove that  $\text{As}^v$  becomes  $\text{As}'''$ , add excess of potassic hydroxide, and then potassium permanganate. The latter will be quickly decolorized.

**Bi<sup>v</sup> n.**  $\text{Bi}_2\text{O}_3$  becomes bismuth oxalate and  $\text{CO}_2$ .

**Mn o.**  $\text{Mn}''^{+n}$  becomes  $\text{Mn}''$ . (That is, all compounds of manganese having more than two bonds are reduced to the dyad.) In absence of other free acid,  $\text{MnC}_2\text{O}_4$  is formed, and  $\text{CO}_2$  is given off. If some non-reducing acid is present, such as  $\text{H}_2\text{SO}_4$ , it unites with the manganese, and all of the oxalic acid is converted into  $\text{CO}_2$ .

**Co''' p.**  $\text{Co}_2\text{O}_3$  and  $\text{Co}_2(\text{OH})_6$  form cobaltous oxalate, and  $\text{CO}_2$  is evolved.

**Ni''' q.** Nickelic oxide and hydroxide become nickelous oxalate, and  $\text{CO}_2$  is evolved.

**Cr<sup>vi</sup> r.** Chromic acid is reduced to chromic oxalate, and  $\text{CO}_2$  is evolved.

## CARBONIC ANHYDRIDE. $\text{CO}_2$ .

### CARBONIC ACID (hypothetical). $\text{H}_2\text{CO}_3$ .

Oxidation valence..... $\text{C}^{\text{iv}}\text{O}^{-\text{ii}}$ ,  $\text{H}'_2\text{C}^{\text{iv}}\text{O}^{-\text{ii}}$

Structural valence..... $\text{O}=\text{C}=\text{O}$ ,  $\text{H}-\text{O}-\overset{\text{O}}{\underset{|}{\text{C}}}-\text{O}-\text{H}$

**660.** The vapor density is 22, indicating that its molecule is  $\text{CO}_2$ . *Specific gravity* of the gas, 1.52. Of the liquid at  $-34^\circ \text{C}$ ., 1.057. At  $-1.6^\circ \text{C}$ ., 0.91; at  $+11^\circ \text{C}$ ., 0.84 (CAILLETET, 1886). *Specific gravity* of solid  $\text{CO}_2$  (hammered), slightly under 1.2 (LANDOLT, 1884).

**661. Occurrence.**—In a free state in the air, about 0.04 per cent. Found in great abundance in the form of carbonates in the earth's crust—*e.g.*, limestone, marble, magnesite, dolomite, etc.

**Preparation.**—For laboratory use, it is usually made by the action of an

acid on some cheap carbonate—*e.g.*, sulphuric acid upon marble. It is produced: (1) In respiration. (2) In fermentation. (3) Decomposition of carbonates by heat, except of alkaline carbonates. (4) By burning carbon, or any material containing carbon, in the air. (5) By reducing metallic oxides by carbon. (6) By the action of steam, at a red heat, upon  $\text{C}$ ,  $\text{CO}$ , or any carbonate (except carbonates of the alkalis, which are not decomposed in this manner).

**662. Properties.**—A heavy, colorless gas, incombustible. A non-supporter of ordinary combustion (used in chemical fire-engines, to extinguish fire), but  $\text{K}$ ,  $\text{Na}$ , and  $\text{Mg}$  burn in the gas, forming free carbon and an oxide of the metal. It is not poisonous, but kills by excluding the air from the lungs. Taken internally is sometimes healthful—*e.g.*, soda-water. At  $17^\circ \text{C}$ . ( $63^\circ \text{F}$ .), a pressure of 54 atmospheres liquefies it. At  $0^\circ \text{C}$ . a pressure of 35 atmospheres liquefies it. If the pressure be removed, the cold produced by its expansion ( $-57^\circ \text{C}$ .) freezes it to a transparent solid, resembling ice. Water at  $15^\circ \text{C}$ . absorbs its own volume of  $\text{CO}_2$ , and undoubtedly forms carbonic acid,  $\text{H}_2\text{CO}_3$ ; but it has not been isolated. In this respect it should be classed with  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{CrO}_4$ ,  $\text{H}_3\text{AsO}_3$ , etc.

The alkali metals form double carbonates with hydrogen, or acid carbonates, as  $\text{KHCO}_3$ . The anhydride,  $\text{CO}_2$ , is often (improperly) designated as carbonic acid.

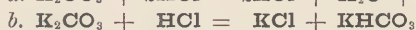
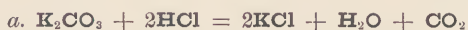
**663. The Carbonates** of the metals of the alkalis are very freely **soluble in water**; the hydrogen carbonates of the same metals, moderately soluble in water. *All other metallic carbonates are insoluble in water.* The carbonates of the alkaline earth metals, and of some others, dissolve slightly in water saturated with carbonic acid, and to a greater extent in water saturated with compressed carbonic acid—from which solutions they are fully precipitated on heating in open vessels. Alcohol dissolves normal ammonium carbonate, but *metallic* carbonates are insoluble in alcohol.

In **analysis**, the carbonates are denoted by the sudden effervescence, etc. (664), caused even by acetic acid.

**664.** The carbonates, both soluble and insoluble, are decomposed by **all the acids** (except hydrosulphuric and hydrocyanic), even when very dilute. The decomposition is attended by *sudden effervescence of carbonic anhydride*,  $\text{CO}_2$ , which reddens moist **litmus** (*a*).

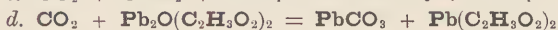
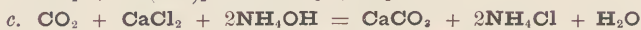
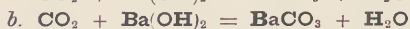
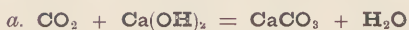
With normal carbonates in cold solution, slight additions of acid (short of a saturation of half the base) do not cause effervescence, because acid carbonate is formed (*b*); and when there is much free alkali present (as in testing caustic alkalis for slight admixtures of carbonate), perhaps no effervescence is obtained. By the time all the alkali is saturated with acid, there is enough water present to dissolve the little quantity of gas set free. But if the carbonate *solution is added drop by drop to the acid*, so that the

latter is constantly in excess, even slight traces of carbonate give notable effervescence.



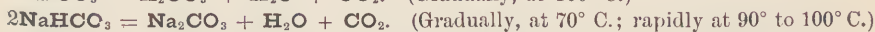
665. The effervescence of carbonic acid gas,  $\text{CO}_2$ , is distinguished from that of  $\text{H}_2\text{S}$  or  $\text{SO}_2$  by the gas being odorless, from that of  $\text{N}_2\text{O}_3$  by its being colorless and odorless; from all others by the effervescence being proportionally more forcible. It should be remembered, however, that  $\text{CO}_2$  is evolved (with  $\text{CO}$ ) on adding strong sulphuric acid to *oxalates* or to *cyanates*.

On passing the gas,  $\text{CO}_2$ , into solution of calcium hydroxide (*a*); or of barium hydroxide (*b*); or into solutions of calcium or barium chloride, containing much ammonium hydroxide (*c*), or into ammoniacal solution of lead acetate (*d*), a white precipitate or turbidity of insoluble carbonate is obtained. In the case of the solution of lime (or of baryta if dilute), the precipitate is soluble in sufficient excess of the gas—*i.e.*, in water saturated with carbonic acid; but it is not easy to saturate with gas generated in an open test-tube. The precipitate may be obtained by *decanting* the gas (one-half heavier than air) from the test-tube in which it is liberated into a (wide) test-tube, containing the solution to be precipitated; but the operation requires a little perseverance, with repeated generation of the gas, owing to the difficulty of displacing the air by pouring into so narrow a vessel. The result is controlled better by generating the gas in a large test-tube, having a stopper bearing a narrow delivery-tube, so bent as to be turned down into the solution to be precipitated.



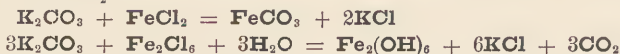
The solutions of calcium and barium hydroxides furnish more delicate tests for carbonic anhydride than the ammoniacal solutions of calcium and barium chlorides, but less delicate than lead basic acetate solution. The latter is so rapidly precipitated by atmospheric carbonic anhydride, that it cannot be preserved in bottles partly full and frequently opened, and cannot be diluted clear, unless with recently boiled water.

666. Solutions of the acid carbonates effervesce, with escape of  $\text{CO}_2$ , on boiling or heating, thus:



667. Solutions of carbonates form precipitates with salts of all metals, except those of the alkalis; the precipitate being, in the larger number

of cases, a carbonate or basic carbonate; in some cases, a hydroxide, with effervescence of  $\text{CO}_2$ :

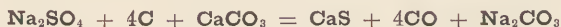


668. On ignition, the normal carbonates of the metals of the fixed alkalies are not decomposed; the carbonates of barium, strontium, and calcium are dissociated slowly, at white heat, forming the oxide and  $\text{CO}_2$ . At a lower temperature, ignition changes all other carbonates to the oxide and  $\text{CO}_2$ , except that the carbonates of silver, mercury, and some of the rarer metals are reduced to the metallic state,  $\text{CO}_2$  and oxygen being evolved.

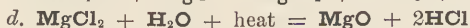
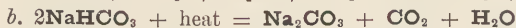
669. To detect free carbonic acid in presence of bicarbonates, a solution of 1 part of rosolic acid in 500 parts of 80 per cent. alcohol may be employed, to which barium hydroxide has been added until it begins to acquire a red tinge. If 0.5 c.c. of this rosolic acid solution is added to about 50 c.c. of the water to be tested—spring water, for instance—the liquid will be colorless, or at most faintly yellowish if it contains free carbonic acid, whereas, if there is no free carbonic acid, but only double salts, it will be red (M. v. PETTENKOFER).

SALZER (*Zeit. Anal. Chem.*, 20, 227) gives a test for free carbonic acid or bicarbonates in presence of carbonates, founded on the fact that the Nessler ammonia reaction (40) does not take place in presence of free carbonic acid or carbonates.

670. Preparation of Carbonates. —  $\text{Na}_2\text{CO}_3$  is made by converting  $\text{NaCl}$  into  $\text{Na}_2\text{SO}_4$ , by treating it with  $\text{H}_2\text{SO}_4$ ; then by long ignition with coal and calcium carbonate, impure sodium carbonate is formed (LEBLANC'S process).



It is separated by lixiviation with water, and farther purified. The other method, known as the ammonia, or Solway's process, consists in passing  $\text{NH}_3$  and  $\text{CO}_2$  into a concentrated solution of  $\text{NaCl}$  (*a*). The  $\text{NaHCO}_3$  is converted into  $\text{Na}_2\text{CO}_3$  by heat, and the evolved  $\text{CO}_2$  used over again (*b*). The  $\text{NH}_4\text{Cl}$  is treated with  $\text{MgO}$  (*c*), and the  $\text{NH}_3$  which is given off is used over again. The  $\text{MgCl}_2$  is strongly heated (*d*) and the  $\text{MgO}$  is used over again, and the evolved gas sold as hydrochloric acid. This continuous process is rapidly superseding the Leblanc process.



The other carbonates are mostly made from the sodium salt.

The normal carbonates of  $\text{Ag}$ ,  $\text{Cd}$ ,  $\text{Mn}''$ ,  $\text{Fe}''$ ,  $\text{Ba}$ ,  $\text{Sr}$ , and  $\text{Ca}$ , may be formed by precipitation with alkaline carbonates, and  $\text{HgCO}_3$  is formed by fixed alkaline, not by ammonium carbonate.

Basic salts are formed by adding alkaline carbonates to solutions of  $\text{Pb}$ ,



**Bi, Cu, Zn, Co, Ni, and Mg.**  $\text{SbCl}_3$  is precipitated as  $\text{Sb}_2\text{O}_3$ , and salts of  $\text{Sn}^{\text{II}}$ ,  $\text{Sn}^{\text{IV}}$ , **Al**,  $(\text{Fe}_2)^{\text{VI}}$ , and  $(\text{Cr}_2)^{\text{VI}}$  as a hydroxide. Fixed alkaline carbonates with  $\text{HgCl}_2$  precipitate a basic chloride, with  $\text{Hg}(\text{NO}_3)_2$  a basic carbonate.

The above carbonates, both the normal and basic, may also be formed by adding  $\text{CO}_2$  to the respective hydroxides.

**Oxidation**—The carbon of  $\text{CO}_2$  cannot be farther oxidized. Hence, it cannot, under any conditions, act as a reducing agent. At a red heat it is reduced to **CO** by carbon or steam; and to free carbon by ignition with **Na, K, or Mg**.

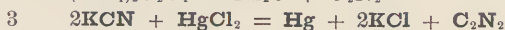
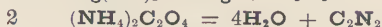
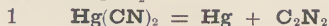
### CYANOGEN. $\text{C}_2\text{N}_2$ .

Oxidation valence..... $\text{C}^{\text{III}}_2\text{N}^{\text{III}}_2$

Structural valence..... $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$

**671.** *Specific gravity* of gas, 1.806 (**GAY-LUSSAC**); of liquid, 0.866 (**FARADAY**, 1845). Vapor density, 26 ( $\text{H}=1$ ), indicating that the molecule is  $\text{C}_2\text{N}_2$ . Not found in nature in a free state.

**Preparation**—(1) By the action of heat upon the cyanides of mercury, silver, or gold. (2) By dry distillation of ammonium oxalate. (3) By fusion of **KCN** with  $\text{HgCl}_2$ .



**Properties**.—A colorless gas, having the odor of bitter almonds. It is intensely poisonous. A pressure of four atmospheres liquefies it at  $7.2^\circ\text{C}$ . In ordinary atmospheric pressure it liquefies at  $-30^\circ\text{C}$ . and freezes at  $-34^\circ\text{C}$ . Water dissolves  $4\frac{1}{2}$ , ether 5, and alcohol 23 volumes of the gas. It burns in the air, giving  $\text{CO}_2$  and free nitrogen. With **KOH** forms **KCN** and **KCNO**.



### HYDROCYANIC ACID. **HCN**.

Oxidation valence..... $\text{H}'\text{C}^{\text{II}}\text{N}^{\text{III}}$

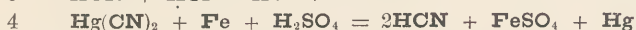
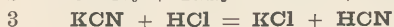
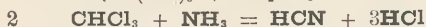
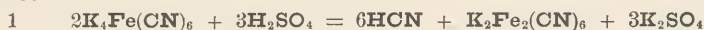
Structural valence..... $\text{H}-\text{C}\equiv\text{N}$

**672.** *Specific gravity* of liquid, at  $18^\circ\text{C}$ ., 0.6969 (**GAY-LUSSAC**). *Specific gravity* of vapor, 0.947. Vapor density ( $\text{H}=1$ ), 13.5. The liquid boils at  $26.5^\circ\text{C}$ . and freezes at  $-15^\circ\text{C}$ . (**GAY-LUSSAC**).

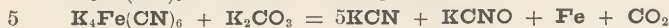
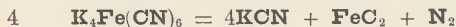
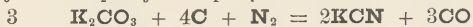
**Occurrence**.—The kernels of bitter almonds, peaches, apricots, plums, cherries, and quinces; the blossoms of the peach, sloe, and mountain-ash; the leaves of the peach, cherry-laurel, and Portugal laurel; the young branches of the peach; the stem-bark of the Portugal laurel and mountain-

ash; and the roots of the last-named tree, when soaked in water and distilled after a while, yield hydrocyanic acid, together with bitter-almond oil.

**673. Preparation.**—(1) By action of dilute sulphuric acid on  $\text{K}_4\text{Fe}(\text{CN})_6$ . (2) By heating chloroform with ammonium hydroxide. (3) By action of acids upon metallic cyanides. (4) By action of  $\text{H}_2\text{SO}_4$  on  $\text{Hg}(\text{CN})_2$  in presence of  $\text{Fe}$ .



**674. Preparation of Metallic Cyanides.**—(1) By action of  $\text{HCN}$  on metallic hydroxides. (2) By action of soluble cyanides on metallic salts. (3)  $\text{KCN}$  may be made by passing nitrogen over a red hot mixture of  $\text{K}_2\text{CO}_3$  and carbon, or (4) by igniting  $\text{K}_4\text{Fe}(\text{CN})_6$ , or (5) heating  $\text{K}_4\text{Fe}(\text{CN})_6$  with  $\text{K}_2\text{CO}_3$ . If prepared in this manner, it contains some cyanate.



**675.** Absolute hydrocyanic acid,  $\text{HCN}$  (formerly called prussic acid), at ordinary temperatures is a colorless liquid, boiling at  $26.5^\circ \text{C}$ . ( $81.5^\circ \text{F}$ .), soluble in all proportions in water, alcohol, and in ether—decomposing slightly in its water solutions, scarcely at all in the dark. It vaporizes from its solutions, the more rapidly as they are more concentrated and at higher temperatures, and distills readily unchanged. It has a characteristic odor presented in a modified form by bitter almonds. The pharmacopœial solution, “diluted hydrocyanic acid” (not Scheele’s), contains two per cent. of the acid. (The vapor, unless greatly diluted with air, is a quick poison by inhalation: antidotes, chlorine or ammonia, by inhalation)

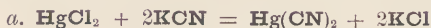
**676.** The **Cyanides** of the alkali metals, alkaline earth metals, and mercuric cyanide, are **soluble in water**—barium cyanide being but sparingly soluble. The solutions are alkaline to test-paper. The other metallic cyanides are insoluble in water. Many of these dissolve in solutions of alkaline cyanides, by combination, as *double metallic cyanides*.

In **analysis**, the most delicate tests for hydrocyanic acid are the productions of color compounds of iron (682, 681). For the silver precipitate, 679.

**677.** There are **Two Classes of Double Cyanides**, both of which are formed when a cyanide is precipitated by an alkali cyanide, and redissolved by excess of the precipitant, as shown in equation *a*.

**Class I.** Double cyanides *which are not affected by alkali hydroxides, but suffer dissociation when treated with dilute acids (b)*. These closely resemble the double iodides (potassium mercuric), and the double sulphides or thioalts (457 *e*, etc.) The most fre-

quently occurring of the double cyanides of this class, which dissolve in water, are given below.



Potassium (or sodium) zinc cyanide,  $\text{K}_2\text{Zn}(\text{CN})_4$  or  $(\text{KCN})_2\text{Zn}(\text{CN})_2$ .

Potassium manganic cyanide (or potassium manganecyanide),  $\text{K}_6\text{Mn}_2(\text{CN})_{12}$ .

Potassium (or sodium) nickel cyanide,  $\text{K}_2\text{Ni}(\text{CN})_4$  or  $(\text{KCN})_2\text{Ni}(\text{CN})_2$ .

Potassium (or sodium) copper cyanide,  $\text{K}_2\text{Cu}(\text{CN})_4$  or  $(\text{KCN})_2\text{Cu}(\text{CN})_2$ .

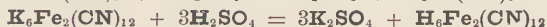
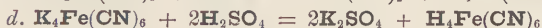
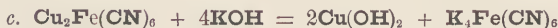
Potassium cadmium cyanide,  $\text{K}_2\text{Cd}(\text{CN})_4$  or  $(\text{KCN})_2\text{Cd}(\text{CN})_2$ .

Potassium (sodium or ammonium) silver cyanide,  $\text{KCNAgCN}$  or  $\text{KAg}(\text{CN})_2$ .

Potassium (or sodium) mercuric cyanide,  $\text{K}_2\text{Hg}(\text{CN})_4$  or  $(\text{KCN})_2\text{Hg}(\text{CN})_2$ .

Potassium (or sodium) auric cyanide,  $\text{KAu}(\text{CN})_4$  or  $\text{KCN Au}(\text{CN})_3$ .

Class II. Double cyanides which, as precipitates, are transposed by alkali hydroxides, in dilute solution (c), and are transposed, without dissociation, by dilute acids (d). In these double cyanides, as potassium ferrous cyanide,  $\text{K}_4\text{Fe}(\text{CN})_6$ , the whole of the cyanogen appears to form a new compound radical with that metal whose single cyanide is insoluble in water; thus,  $\text{Fe}(\text{CN})_6$  as "ferrocyanogen," giving  $\text{K}_4\text{Fe}(\text{CN})_6$  as "potassium ferrocyanide" (for the potassium ferrous cyanide). These more stable double cyanides or "ferrocyanides," etc., correspond to the platinic double chlorides or "chloroplatينات" (587), and the palladium double chlorides, or chloropalladiates (595). The most frequently occurring of the double cyanides of this class, which are soluble in water, are given below.



Alkali ferrocyanides, as  $\text{K}_4\text{Fe}''(\text{CN})_6$ , potassium ferrous cyanide.

Ferricyanides, as  $\text{K}_6\text{Fe}_2^{\text{VI}}(\text{CN})_{12}$ , potassium ferric cyanide.

Cobalticyanides, as  $\text{K}_6(\text{Co}_2)^{\text{VI}}(\text{CN})_{12}$ , potassium cobaltic cyanide.

Manganicyanides, as  $\text{K}_6(\text{Mn}_2)^{\text{VI}}(\text{CN})_{12}$ , potassium manganic cyanide.

Chromicyanides, as  $\text{K}_6(\text{Cr}_2)^{\text{VI}}(\text{CN})_{12}$ , potassium chromic cyanide.

The easily decomposed double cyanides of Class I. are, like the single cyanides, intensely poisonous. The difficultly decomposed double cyanides of Class II. are not poisonous.

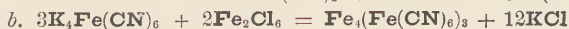
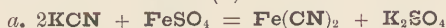
678. The **Single Cyanides** are transposed by the stronger mineral acids, more or less readily, with liberation of *hydrocyanic acid*,  $\text{HCN}$ , effervescing from concentrated or hot solutions, remaining dissolved in cold and dilute solutions. Mercuric cyanide furnishes  $\text{HCN}$  by action of  $\text{H}_2\text{S}$ , not by other acids. The cyanides of the alkali and alkaline earth metals are transposed by all acids—even the carbonic acid of the air—and exhale the odor of hydrocyanic acid.

679. Solution of silver nitrate precipitates, from solutions of cyanides or of hydrocyanic acid (not from mercuric cyanide) *silver cyanide*,  $\text{AgCN}$ , white, insoluble in dilute nitric acid, soluble in ammonium hydroxide, in hot ammonium carbonate, in potassium cyanide, and in thiosulphates—uniform with silver chloride. Cold strong hydrochloric acid decomposes it with evolution and odor of hydrocyanic acid (recognition *from chloride*);

and when well washed, and then gently ignited, it does not melt, but leaves metallic silver, soluble in dilute nitric acid, and precipitable as chloride (distinction and means of separation from chloride).

**680.** Solution of **mercurous nitrate**, with cyanides or hydrocyanic acid, is resolved into *metallic mercury*, as a gray precipitate, and mercuric cyanide and nitrate, in solution. Salts of **copper** react, as stated in 344; salts of **lead**, as stated in 395.

**681.** **Ferrous salts**, added to saturation, precipitate from solutions of cyanides, not from hydrocyanic acid, *ferrous cyanide*,  $\text{Fe}(\text{CN})_2$ , white, if free from the ferric hydroxide formed by admixture of ferric salt, and, with the same condition, soluble in excess of the cyanide, as (with potassium cyanide),  $(\text{KCN})_2\text{Fe}(\text{CN})_2 = \text{K}_4\text{Fe}(\text{CN})_6$ , potassium *ferrocyanide* (a). On acidulating this solution, it gives the blue precipitates with iron salts, more marked with ferric salts (b):



This production of the blue ferric ferrocyanide is made a delicate test for hydrocyanic acid, as follows: A little potassium hydroxide and ferrous sulphate are added, the mixture digested warm for a short time; then a very little ferric chloride is added, and the whole slightly acidulated (so as to dissolve all the ferrous and ferric hydroxides), when prussian blue will appear, if hydrocyanic acid was present.

**682.** The production of the red ferric thiocyanate is a test for hydrocyanic acid, more delicate than formation of ferrocyanide. By warm digestion this reaction occurs:  $2\text{KCN} + \text{S}_2 = 2\text{KCNS}$ ; or:



To the material in an evaporating-dish, add one or two drops of **yellow ammonium sulphide**, and digest on the water-bath until the mixture is colorless, and free from sulphide. Slightly acidulate with hydrochloric acid (which should not liberate  $\text{H}_2\text{S}$ ), and add a drop of solution of ferric chloride; the blood-red solution of ferric thiocyanate will appear, if hydrocyanic acid was present.

**683.** Solution of **nitrophenic acid**,  $\text{C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$ , added, in a small quantity, to a neutralized solution of cyanides of alkali metals, on boiling (and standing), gives a blood-red color, due to picrocyanate (as  $\text{KC}_8\text{H}_4\text{N}_5\text{O}_6$ ). This test is very delicate, but not very distinctive, as various reducing agents give red products with nitrophenic acid.

**684.** The **fixed alkali hydroxides**, in boiling solution, strongly alkaline, gradually decompose the cyanides with production of *ammonia* and formate. Ferrocyanides and ferriecyanides finally yield the same products. Dilute alkalies, not heated, transpose, as by equation c, 677.



By fusion with alkali hydroxides, all cyanogen compounds yield ammonia. **Concentrated sulphuric acid** decomposes cyanogen in all of its compounds.



**685.** Cyanides are **Reducing Agents**—in the wet way having a moderate, in the dry way a forcible action ; and in either way removing sulphur, as well as oxygen :

With oxides :  $\text{O} + \text{KCN} = \text{KCNO}$

With sulphides :  $\text{S} + \text{KCN} = \text{KCNS}$

In solution : cyanides decolorize the **permanganate**, but do not reduce the cupric hydroxide with potassium hydroxide.

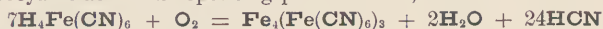
By fusion : cyanides are employed as the most efficient of agents for obtaining metals from their oxides or sulphides, as has been stated with reference to arsenic, tin, etc. The cyanates and thiocyanates, so formed, are not readily decomposed by heat alone.

By exposure to the air, cyanides acquire some proportion of cyanates, and commercial cyanide of potassium contains cyanate.

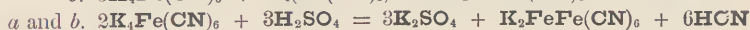
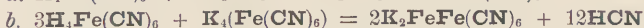
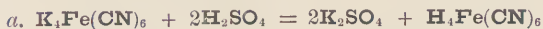
### FERROCYANIC ACID. $\text{H}_4\text{Fe}(\text{CN})_6$ .

Oxidation valence....  $\text{H}'\text{Fe}''(\text{C}''\text{N}''')_6^*$

**686.** Absolute ferrocyanic acid, frequently called hydroferrocyanic acid,  $\text{H}_4\text{Fe}(\text{CN})_6$ —see 677, Class II.—is a white solid, freely soluble in water and in alcohol. The solution is strongly acid to test-paper, and decomposes carbonates with effervescence, and acetates. It is non-volatile, but absorbs oxygen from the air, more rapidly when heated, evolving hydrocyanic acid and depositing prussian blue, thus:



**687.** Ferrocyanic acid is formed by transposition of metallic ferrocyanides in solution, with strong acids (*a*). When the solution is heated, hydrocyanic acid is evolved; in the case of an alkali ferrocyanide, without absorption of oxygen (*b*). Potassium ferrocyanide and sulphuric acid are usually employed for preparation of hydrocyanic acid:



**688.** The **Ferrocyanides** of the alkali metals, strontium, calcium, and magnesium, are freely soluble in water; of barium, sparingly soluble; of the other metals, insoluble in water. There are *double ferrocyanides*; soluble and insoluble; that of barium and potassium is soluble, but *potassio calcic ferrocyanide* is insoluble. The most of the ferrocyanides of a heavy metal and an alkali metal are insoluble. Potassium and sodium ferrocyanides are precipitated from their water solutions by alcohol (distinction from ferricyanides).

The soluble ferrocyanides are yellowish in solution and in crystals, white when anhydrous. The *insoluble ferrocyanides* have marked and very diverse colors—as seen below.

In **analysis**, soluble ferrocyanides are recognized by their reactions with ferrous and ferric salts and copper salts (689). Separated from ferricyanide, by insolubility of alkali salt in alcohol.

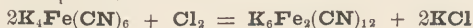
**689.** Solutions of alkali **Ferrocyanides**, as  $\text{K}_4\text{Fe}(\text{CN})_6$ , give, with soluble salts of :

\* Upon structural formulæ of the ferrocyanides and ferricyanides see *Ladenburg's Handwörterbuch* (1885) III. 83, 98.

Aluminium, a white precipitate,	$\text{Al}_2(\text{OH})_6$ and $\text{Fe}(\text{CN})_2$ (formed slowly).
Antimony, a white	“
Bismuth, a white	“ $\text{Bi}_4(\text{Fe}(\text{CN})_6)_3$ .
Cadmium, a white	“ $\text{Cd}_2\text{Fe}(\text{CN})_6$ (sol. in hydrochloric acid).
Calcium, a white	“ $\text{K}_2\text{CaFe}(\text{CN})_6$ .
Chromium, no	“
Cobalt, a green, then gray	“ $\text{Co}_2\text{Fe}(\text{CN})_6$ .
Copper, a red-brown	“ $\text{Cu}_2\text{Fe}(\text{CN})_6$ .
Gold, no	“
Iron (ferrous), whi. then blue	“ $\text{K}_2\text{FeFe}(\text{CN})_6$ .
Iron (ferric), a deep blue	“ $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ .
Lead, a white	“ $\text{Pb}_2\text{Fe}(\text{CN})_6$ .
Magnesium, a white	“ $(\text{NH}_4)_2\text{MgFe}(\text{CN})_6$ (in presence of $\text{NH}_4$ ).
a yellow-white	“ $\text{K}_2\text{MgFe}(\text{CN})_6$ (only in conc. solution).
Manganese, a white	“ $\text{Mn}_2\text{Fe}(\text{CN})_6$ (sol. in hydrochloric acid).
Mercury (mercurous), a whi.	“ $\text{Hg}_4\text{Fe}(\text{CN})_6$ (gelatinous).
Mercury (mercuric), a white	“ $\text{Hg}_2\text{Fe}(\text{CN})_6$ , turning to $\text{Hg}(\text{CN})_2$ and $\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$ , blue.
Molybdenum, a brown	“
Nickel, a greenish-white	“ $\text{Ni}_2\text{Fe}(\text{CN})_6$ .
Silver, a white	“ $\text{Ag}_4\text{Fe}(\text{CN})_6$ , (slowly turning blue).
Tin (stannous, stannic), whi.	“ (gelatinous).
Uranium (uranous), brown	“ $\text{UFe}(\text{CN})_6$ .
Uranium (uranic), red-brown	“ $\text{U}_2(\text{Fe}(\text{CN})_6)_3$ .
Zinc, a white, gelatinous	“ $\text{Zn}_2\text{Fe}(\text{CN})_6$ .

Insoluble ferrocyanides are transposed by alkalis (677 c, and 684).

690. It will be observed (677) that *ferrocyanides* are *ferrous* combinations, while *ferricyanides* are *ferric* combinations. And, although ferrocyanides are far less easily oxidized than simple ferrous salts, being stable in the air, they are nevertheless **reducing-agents**—of moderate power.



#### 691. Oxidation.—

$\text{HNO}_2$  a. Forms first ferricyanic acid, then nitroferricyanic acid and  $\text{NO}$ .

$\text{HNO}_3$  b. Forms ferricyanic acid, and then nitroferricyanic acid,  $\text{NO}$  being evolved.

$\text{Cl}$  c. Forms first ferricyanic and hydrochloric acids. Excess of chlorine to be avoided in preparation of ferricyanides.

- $\text{HClO}_3$  *d.* Forms ferricyanic acid and  $\text{HCl}$ .  
 $\text{Br}$  *e.* Forms ferricyanic and hydrobromic acids.  
 $\text{HBrO}_3$  *f.* Forms ferricyanic and hydrobromic acids.  
 $\text{I}$  *g.* Iodine is decolorized by potassium ferrocyanide, and some potassium ferricyanide and potassium iodide are formed. The action is slow and never complete (*Gmelin's Hand-book*, 7, 459).  
 $\text{HIO}_3$  *h.* Forms ferricyanic acid and free iodine.  
 $\text{PbO}_2$  *i.* With sulphuric acid forms  $\text{Pb}''$  and ferricyanic acid.  
 $\text{Ag}'$  *j.* With fixed alkali, forms an alkaline ferricyanide and metallic silver.  
 $\text{MnO}_2$  *k.* With phosphoric acid, gives  $\text{Mn}''$  and ferricyanic acid.  
 $\text{Mn}^{\text{VII}}$  *l.* Forms with potassium hydroxide  $\text{MnO}_2$  and potassium ferricyanide. With sulphuric acid, manganous sulphate and ferricyanic acid.  
 $\text{Co}'''$  *m.* With phosphoric acid, forms  $\text{Co}''$  and ferricyanic acid.  
 $\text{Ni}'''$  *n.* With acetic acid, gives  $\text{Ni}''$  and ferricyanic acid.  
 $\text{Cr}^{\text{VI}}$  *o.* With phosphoric acid, gives  $\text{Cr}'''$  and ferricyanic acid (*Schönbein, Jour. für Pract. Chemie*, 20, 145).

### FERRICYANIC ACID. $\text{H}_6\text{Fe}_2(\text{CN})_{12}$

Oxidation valence..... $\text{H}'_6\text{Fe}'''_2(\text{C}'''\text{N}''')_{12}$

692. Absolute ferricyanic acid (quite as frequently called hydroferricyanic acid),  $\text{H}_6\text{Fe}_2(\text{CN})_{12}$ , is a non-volatile, crystallizable solid, readily soluble in water, with a brownish color, and an acid reaction to test-paper. It is decomposed by a slight elevation of temperature. In the transposition of most ferricyanides, by sulphuric or other acid, the hydroferricyanic acid radical is broken up.

693. The **Ferricyanides** of the metals of the alkalis and alkaline earths are **soluble in water**; those of most of the other metals are insoluble or sparingly soluble. Potassium and sodium ferricyanides are but slightly, or not at all, precipitated from their water solutions by **alcohol** (separation from ferrocyanides).

In **analysis**, the reactions with ferrous and ferric salts are distinguishing.

The soluble ferricyanides have a red color, both in crystals and solution; those insoluble have different, strongly marked colors.

Ferricyanides are not easily decomposed by dilute acids; but alkali hydrates either transpose them (677 *c*), or decompose their radicals (684).

Solutions of metallic **Ferricyanides** give, with soluble salts of :

**Aluminium**, no precipitate.

**Antimony**, no precipitate.

**Bismuth**, light-brown precipitate,  $\text{Bi}_2\text{Fe}_2(\text{CN})_{12}$ —insol. in hydrochloric acid.

**Cadmium**, yellow precipitate,  $\text{Cd}_3\text{Fe}_2(\text{CN})_{12}$ —sol. in acids and in ammonia.

**Chromium**, no precipitate.

**Cobalt**, brown-red precipitate,  $\text{Co}_3\text{Fe}_2(\text{CN})_{12}$ —insoluble in acids. With ammonium chloride and hydroxide, excess of ferricyanide gives a blood-red solution, a distinction of cobalt, from nickel, manganese and zinc.

**Copper**, a yellow-green precipitate,  $\text{Cu}_3\text{Fe}_2(\text{CN})_{12}$ —insol. in hydrochl. acid.

**Gold**, no precipitate.

**Iron (ferrous)**, dark blue precipitate,  $\text{Fe}_3\text{Fe}_2(\text{CN})_{12}$ —insoluble in acids.

**Iron (ferric)**, no precipitate, a darkening of the liquid.

**Lead**, no precipitate, except in concentrated solutions (dark brown).

**Manganese**, brown precipitate,  $\text{Mn}_3\text{Fe}_2(\text{CN})_{12}$ —insoluble in acids.

**Mercury (Mercurous)**, red-brown precipitate, turning white on standing.

**Mercury (mercuric)**, no precipitate.

**Nickel**, yellow-green precipitate,  $\text{Ni}_3\text{Fe}_2(\text{CN})_{12}$ —insol. in hydrochloric acid.

With ammonium chloride and hydroxide, excess of ferricyanide gives a copper-red precipitate.

**Silver**, a red-brown precipitate,  $\text{Ag}_3\text{Fe}_2(\text{CN})_{12}$ —soluble in ammonia.

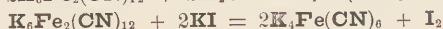
**Tin (stannous)**, white precipitate,  $\text{Sn}_3\text{Fe}_2(\text{CN})_{12}$ —sol. in hydrochloric acid.

**Tin (stannic)**, no precipitate.

**Uranium (uranous)**, no precipitate.

**Zinc**, orange precipitate,  $\text{Zn}_3\text{Fe}_2(\text{CN})_{12}$ —soluble in hydrochloric acid and in ammonia.

**694.** Ferricyanides, as *ferric* combinations, are capable of acting as **Oxidizing Agents**, the radical  $\text{Fe}''_2(\text{C}''\text{N}''')_{12}$ , becoming  $\text{Fe}''(\text{C}''\text{N}''')_6$ , and taking another portion of metal into combination, forming ferrocyanides (compare 690).



**Nitric acid**, or acidulated nitrite, by continued digestion in hot solution, effects a still higher **Oxidation of Ferricyanides**, with the production, among other products, of *nitro-ferricyanides* or *nitro-prussides*. These salts are generally held to have the composition represented by the acid  $\text{H}_2\text{Fe}(\text{NO})(\text{CN})_5$ . *Sodium Nitroprusside* is used as a reagent for soluble sulphides—that is, in presence of alkali hydroxides, a test for hydrosulphuric acid; in presence of hydrosulphuric acid, a test for alkali hydroxides.

#### Oxidation.—

$\text{HNO}_2$  *a.* Forms nitroferricyanic acid.

$\text{HNO}_3$  *b.* Forms nitroferricyanic acid.

$\text{H}_3\text{PO}_2$  *c.* Forms ferrocyanic acid and  $\text{H}_3\text{PO}_4$ .

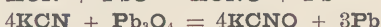
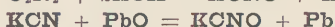
$\text{H}_2\text{S}$  *d.* Forms ferrocyanic acid and sulphur.



- $\text{H}_2\text{SO}_3$  *e.* Forms ferrocyanic acid and  $\text{H}_2\text{SO}_4$ .  
 $\text{Cl}$  *f.* Decomposes, forming various undetermined products.  
 $\text{HClO}_3$  *g.* Chloric acid acts upon potassium ferricyanide, forming potassium super-ferricyanide,  $\text{K}_2\text{Fe}(\text{CN})_6$ .  
 $3\text{K}_2\text{Fe}_2(\text{CN})_{12} + \text{KClO}_3 + 6\text{HCl} = 6\text{K}_2\text{Fe}(\text{CN})_6 + 7\text{KCl} + 3\text{H}_2\text{O}$  (Z. H. SKRAUP).  
 $\text{HI}$  *h.* Forms ferrocyanic acid and free iodine.  
 $\text{Pb}''$  *i.* With potassium hydroxide, forms  $\text{PbO}_2$  and potassium ferrocyanide [*Watts' Dictionary*, 2, 248].  
 $\text{Sn}''$  *j.* With potassium hydroxide, forms potassium stannate,  $\text{K}_2\text{SnO}_3$ , and potassium ferrocyanide [*Watts' Dictionary*, 2, 248].  
 $\text{Mn}''$  *k.* With potassium hydroxide, forms  $\text{MnO}_2$  and potassium ferrocyanide [*Boudault, Jour. für Prakt. Chemie*, 36, 23].  
 $\text{Cr}'''$  *l.* Forms in alkaline mixture a chromate and a ferrocyanide [*Boudault, Jour. de Pharmacie* (3), 7, 437].

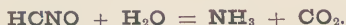
CYANIC ACID.  $\text{HCNO}$ .Oxidation valence . . . . .  $\text{H}'\text{C}^{\text{IV}}\text{N}^{\text{---}}\text{O}^{\text{---}}$ Structural valence . . . . .  $\text{H}-\text{O}-\text{C}\equiv\text{N}$ 

695. The cyanates of the alkalis and of the fourth-group metals may be made by passing cyanogen gas into the hydroxides. The cyanates of the alkalis are easier prepared by fusion of the cyanide with some easily reducible oxide.

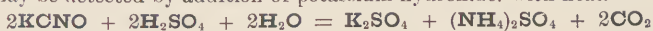


The free acid may be obtained by heating cyanuric acid,  $\text{H}_3\text{C}_3\text{N}_3\text{O}_3$ , to redness, better in an atmosphere of  $\text{CO}_2$ . Cyanic acid is found in the distillate.  $\text{H}_3\text{C}_3\text{N}_3\text{O}_3 = 3\text{HCNO}$ .

Absolute cyanic acid,  $\text{HCNO}$ , is a colorless liquid, giving off pungent, irritating vapor, and only preserved at very low temperatures. It cannot be formed by transposing metallic cyanates with the stronger acids in the presence of water, by which it is changed into carbonic anhydride and ammonia :



696. The Cyanates, therefore, when treated with hydrochloric or sulphuric acid, effervesce with the escape of *carbonic anhydride* (distinction from cyanides), the pungent odor of cyanic acid being perceptible. The ammonia remains in the liquid as ammonium salt, and may be detected by addition of potassium hydroxide, with heat.



697. The cyanates of the metals of the alkalis and of calcium are soluble in water ; most of the others are insoluble or sparingly soluble. All the solutions gradually decompose, with evolution of ammonia.—*Silver cyanate* is sparingly soluble in hot water, readily soluble in ammonia ; soluble, with decomposition, in dilute nitric acid (distinction from cyanide). *Copper cyanate* is precipitated greenish-yellow.

*Ammonium cyanate* in solution changes gradually, or immediately when boiled, to *urea*, or carbamide, with which it is isomeric :  $\text{NH}_4\text{CNO} = (\text{NH}_2)_2(\text{CO})''$ . The latter is recognized by the characteristic crystalline laminae of its nitrate, when a few drops of the solution, on glass, are treated with a drop of nitric acid. Also, solution of *urea* with solution of mercuric nitrate, forms a white precipitate,  $\text{CH}_4\text{N}_2\text{O}(\text{HgO})_2$ , not turned yellow (decomposed) by solution of sodium carbonate (no excess of mercuric nitrate being taken). Solution of *urea*, on boiling, is resolved into ammonium carbonate, which slowly vaporizes :



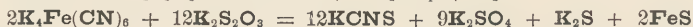
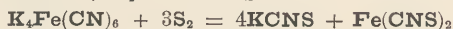
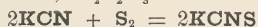
Cyanates, in the dry way, are reduced by strong deoxidizing agents to cyanides.

### THIOCYANIC ACID. HCNS.

Oxidation valence..... $\text{H}'\text{C}^{\text{IV}}\text{N}^{\text{—III}}\text{S}^{\text{—II}}$

Structural valence..... $\text{H}-\text{S}-\text{C}\equiv\text{N}$

698. An aqueous solution of **HCNS** may be obtained by treating lead thiocyanate suspended in water with  $\text{H}_2\text{S}$ . Also treating barium thiocyanate with  $\text{H}_2\text{SO}_4$  in molecular proportions. The anhydrous acid is obtained by treating dry  $\text{Hg}(\text{CNS})_2$  with  $\text{H}_2\text{S}$ . Potassium thiocyanate is formed by fusing **KCN** with **S**. Or two parts of  $\text{K}_4\text{Fe}(\text{CN})_6$  with one part of sulphur. Also by fusing the cyanide, or ferrocyanide of potassium with potassium thiosulphate,  $\text{K}_2\text{S}_2\text{O}_3$ .



Thiocyanic is quite as frequently called sulphocyanic acid, and its salts either sulphocyanides or sulphocyanates. It corresponds to cyanic acid, **HCNO**, oxygen being substituted for sulphur.

699. Absolute thiocyanic acid, **HCNS**, is a colorless liquid, crystallizing at  $12^\circ \text{C}$ . ( $54^\circ \text{F}$ .), and boiling at  $85^\circ \text{C}$ . ( $185^\circ \text{F}$ .) It has a pungent, acetous odor, and reddens litmus. It is soluble in water. The absolute acid decomposes quite rapidly at ordinary temperatures; the dilute solution, slowly; with evolution of carbonic anhydride, carbon disulphide, hydrosulphuric acid, hydrocyanic acid, ammonia, and other products.

The same products result, in greater or less degree, from transposing *soluble thiocyanates* with strong acids; in greater degree as the acid is stronger and heat applied; while in dilute cold solution, the most of the thiocyanic acid remains undecomposed, giving the acetous odor (see 701). The thiocyanates, *insoluble* in water, are not all readily transposed. Thiocyanates of metals, whose sulphides are insoluble in certain acids, resist the action of the same acids.

The thiocyanates of the metals of the alkalies, alkaline earths; also, those of iron (ferrous and ferric), manganese, zinc, cobalt, and copper—are **soluble in water**. Mercuric thiocyanate, sparingly soluble; potassio mercuric thiocyanate, more soluble. *Silver thiocyanate* is insoluble in water,

insoluble in dilute nitric acid, slowly soluble in ammonium hydroxide. The ferric reaction is the most **distinctive**.

**700.** Solutions of metallic **Thiocyanates** give, with soluble salts of :

**Cobalt**, very concentrated, a blue color,  $\text{Co}(\text{CNS})_2$ , crystallizable in blue needles, soluble in alcohol, not in carbon disulphide. The coloration is promoted by warming, and the test is best made in an evaporating dish. In strictly neutral solutions, iron, nickel, zinc, and manganese, do not interfere (SCHOENN).

**Copper**, if concentrated, a black crystalline precipitate,  $\text{Cu}(\text{CNS})_2$ , soluble in thiocyanate. With **sulphurous acid**, a white precipitate,  $\text{CuCNS}$ .

**Iron (ferrous)**, no precipitate or color.

**Iron (ferric)**, an intensely blood-red solution of  $\text{Fe}_2(\text{CNS})_6$ , decolored by solution of **mercuric chloride** (217, *distinction from acetic acid*) ; decolored by phosphoric, arsenic, oxalic, and iodic acids, etc., unless with excess of ferric salt ; decolored by alkalis, and by nitric acid, not by dilute hydrochloric acid. On introduction of metallic zinc, it evolves hydrosulphuric acid. Ferric thiocyanate is soluble in **ether**, which extracts traces of it from aqueous mixtures, rendering its color much more evident by the concentration in the ether layer.

**Lead**, gradually, a yellowish crystalline precipitate,  $\text{Pb}(\text{CNS})_2$ , changed by boiling to white basic salt.

**Mercury (mercurous)**, a white precipitate,  $\text{Hg}_2(\text{CNS})_2$ , resolved by boiling into  $\text{Hg}$  and  $\text{Hg}(\text{CNS})_2$ . The mercurous thiocyanate,  $\text{Hg}_2(\text{CNS})_2$ , swells greatly *on ignition* (being used in "Pharaoh's serpents"), with evolution of mercury, nitrogen, thiocyanogen, cyanogen, and sulphur dioxide.

**Mercury (mercuric)**, in solutions not very dilute, a white precipitate  $\text{Hg}(\text{CNS})_2$ , somewhat soluble in excess of the thiocyanates, sparingly soluble in water, moderately soluble in alcohol. On ignition, it swells like the mercurous precipitate.

**Platinum**. Platinic chloride, gradually added to a hot, concentrated solution of potassic thiocyanate, forms a deep-red solution of double thiocyanate of potassium and platinum  $(\text{KCNS})_2\text{Pt}(\text{CNS})_4$ , or more properly,  $\text{K}_2\text{Pt}(\text{CNS})_6$ , the *thiocyano-platinate of potassium*. The latter salt gives bright-colored precipitates with metallic salts. The thiocyano-platinate of lead (so formed) is golden-colored ; that of silver, orange-red.

**Silver**, a white precipitate,  $\text{AgCNS}$ , insoluble in water, insoluble in dilute nitric acid, slowly soluble in ammonium hydroxide, readily soluble in excess of potassic thiocyanate ; blackens in the light.

**701.** Certain active oxidizing agents, viz.: nascent chlorine, and nitric acid containing nitrogen oxides, acting in hot, concentrated solution of thiocyanates, precipitate *perthiocyanogen*,  $\text{H}(\text{CNS})_2$ , of a yellow-red to rose-red color, even blue sometimes, when concentrated. It may be formed in the test for iodine, and mistaken for that element, in starch or carbon disulphide. If boiled with solution of potassium hydroxide, it forms thiocyanate.

Concentrated hydrochloric acid, or sulphuric acid, added in excess to water solution of thiocyanates, causes the gradual formation of a yellow precipitate, *perthiocyanic acid*,  $(\text{HCN})_2\text{S}_2$ , slightly soluble in hot water, from which it crystallizes in yellow needles. It dissolves in alcohol and in ether.

Thiocyanate of potassium can be fused in close vessels, without decomposition; but with free access of air, it is resolved into sulphate and cyanate, with evolution of sulphurous acid.

**702. Oxidation.**—When thiocyanic acid is oxidized, the final product, as far as the sulphur is concerned, is always sulphuric acid or a sulphate. In many cases (in acid mixture) it has been proven that the cyanogen is evolved as hydrocyanic acid. In other cases the same reaction is assumed as probable.

$\text{HNO}_2$  a. Forms sulphuric acid and nitric oxide.

$\text{HNO}_3$  b. Forms sulphuric acid and nitric oxide.

$\text{Cl}$  c. Forms at first a red compound of unknown composition, then  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HCN}$  are produced. In alkaline mixture a chloride and sulphate are formed.

$\text{HClO}$  d. Same as with  $\text{Cl}$ .

$\text{HClO}_2$  e. Forms sulphuric, hydrochloric, and hydrocyanic acids.

$\text{Br}$  f. Forms  $\text{HBr}$  and  $\text{H}_2\text{SO}_4$ ; but with alkalies, a bromide and sulphate.

$\text{HBrO}_3$  g. Forms  $\text{HBr}$  and  $\text{H}_2\text{SO}_4$ .

$\text{HIO}_3$  h. Forms  $\text{H}_2\text{SO}_4$  and free iodine.

$\text{PbO}_2$  and  $\text{Pb}_2\text{O}_4$  i. Forms  $\text{Pb}''$  and sulphuric acid. In acid mixture only (E. A. HARLOW, *Jour. Chem. Soc.*, 11, 174).

$\text{H}_3\text{AsO}_4$  j. Forms  $\text{H}_3\text{AsO}_3$ , hydrocyanic and sulphuric acids.

$(\text{Co}_2)^{\text{VI}}$  k. Forms  $\text{Co}''$ , hydrocyanic and sulphuric acids.

$(\text{Ni}_2)^{\text{VI}}$  l. Forms  $\text{Ni}''$ , hydrocyanic and sulphuric acids.

$\text{Cr}^{\text{VI}}$  m. Forms  $(\text{Cr}_2)^{\text{VI}}$ , hydrocyanic and sulphuric acids.

$\text{Mn}'' + n$  n. Forms  $\text{Mn}''$ , hydrocyanic and sulphuric acids. In alkaline mixture, a cyanate and sulphate are formed (WURTZ'S *Dict. Chim.* 3, 95).

#### NITROGEN. N = 14.0210.

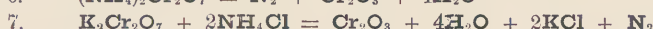
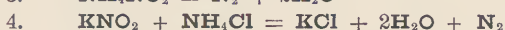
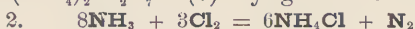
**703. Specific gravity**, 0.9713. Vapor density ( $\text{H} = 1$ ), 14; which is understood to indicate that the molecule has two atoms,  $\text{N}_2$ .

**Occurrence.**—It exists in a free state in the air to the extent of about



79 per cent. by volume. It is found combined with hydrogen as  $\text{NH}_3$ , and with bases as nitres. It exists in combination in the vegetable kingdom in nearly all the products of plant life, and in the animal kingdom in the fluids and tissues of the body.

**Preparation.**—Nitrogen is produced : (1) From the air, by removing the oxygen by ignition of phosphorus, by action of moist iron or other metallic filings, by potassium pyrogallate by  $\text{NO}$  and subsequent washing. (2) By passing  $\text{Cl}$  into an *excess* of  $\text{NH}_4\text{OH}$  solution. (3) By igniting  $\text{NH}_4\text{NO}_2$ . (4) By igniting mixed  $\text{KNO}_2$  and  $\text{NH}_4\text{Cl}$ . (5) By fusing together  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  and washing to remove the chlorine. (6) By ignition of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ . (7) By ignition of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{NH}_4\text{Cl}$ .



**704. Properties.**—A colorless, tasteless, odorless gas. It is not poisonous, but kills by excluding the air from the lungs. It has been liquefied by the cold produced by its own expansion from a compression of 300 atmospheres at  $13^\circ \text{C}$ . Under ordinary atmospheric pressure, liquid nitrogen boils at  $-193.1^\circ \text{C}$ . (WROBLEWSKI, 1884). It rarely combines with other free elements. Quantitatively it is estimated by measuring its volume after separating it from other gases.

**705.** The *Nitrogen Series of Elements* comprises five perissads, all acting as triads in their more stable or typical unions, and differing from each other in regular gradation. Some of these progressive variations may be stated as follows:

	N Non-metal.	P Non-metal.	As Non-metal.	Sb Metal.	Bi Metal.
Atomic weights	14.0210	30.958	74.918	119.955	207.523
Vaporization.	(Gaseous.)	At $287.3^\circ \text{C}$ .	At $450^\circ \text{C}$ .	At white heat.	At full furnace heat.
Typical hydrides.	$\text{N}''' \text{H}_3$ Strong base. Slowly decomposed by electricity.	$\text{P}''' \text{H}_3$ Weak base. Readily decomposed by electricity.	$\text{As}''' \text{H}_3$ Indifferent. Decomposed by red heat.	$\text{Sb}''' \text{H}_3$ Indifferent. Decomposed below red heat.	
Typical oxygen compounds.	$\text{HN}^\vee \text{O}_3$  Active acid. Soluble salts.	$\text{HP}^\vee \text{O}_3$ $\text{H}_3\text{P}^\vee \text{O}_4$ Weak acid. Precipitates.	$\text{H}_3\text{As}^\vee \text{O}_4$ $\text{As}''' \text{O}_3$ Weak acid. Precipitates.	$\text{Sb}''' \text{O}_3$  Indifferent acid. Precipitates.	$\text{Bi}''' \text{O}_3$  Not acidulous. Precipitates.

When any dry carbon-compound containing nitrogen (organic) is heated with excess of dry sodium hydrate and lime (or any dry, fixed alkali), *ammonia* is evolved, and may be recognized by its odor, effect on moist litmus-paper, etc.

NITROUS OXIDE.  $\text{N}_2\text{O}$ .Oxidation valence..... $\text{N}'_2\text{O}''$ Structural valence, usually represented as  $\text{N}=\overset{\text{O}}{\text{N}}$ 

706. *Specific gravity* (observed), 1.614 (DALTON). *Vapor density* ( $\text{H}=1$ ), 22.

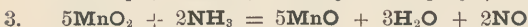
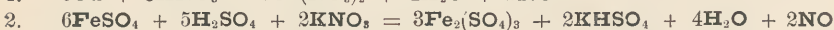
Prepared usually by heating ammonium nitrate to  $243^\circ \text{C}$ . Above  $260^\circ \text{C}$ ., other products, especially  $\text{NO}$ , are formed. It is purified by passing through  $\text{KOH}$ , to remove  $\text{Cl}$ , and through  $\text{FeSO}_4$ , to remove  $\text{NO}$ .

**Properties.**—Nitrous oxide (laughing gas) is colorless, odorless, and has a sweet taste. When inhaled, produces first transient intoxication, and then complete anæsthesia. At  $0^\circ \text{C}$ ., under a pressure of 30 atmospheres, it condenses to a liquid, which, at ordinary atmospheric pressure, boils at  $-92^\circ \text{C}$ . (PICTET). On exposure to the air, the cold caused by its own evaporation causes it to freeze at  $-99^\circ \text{C}$ . (WILLS). Soluble in water, alcohol, and ether. Incombustible, but supports combustion.

NITRIC OXIDE.  $\text{NO}$ .Oxidation valence..... $\text{N}''\text{O}''$ Structural valence...  $-\text{N}=\text{O}$  (FRANKLAND) or  $\overset{\text{O}}{\text{N}}=\text{O}$ 

707. *Specific gravity* 1.041 (THOMSON). *Vapor density*, ( $\text{H}=1$ ), 15.

**Preparation.**—(1) By action of  $\text{HNO}_3$ , sp. gr. 1.20, upon metallic  $\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Hg}$ ,  $\text{Zn}$ , etc. (2) By action of  $\text{FeSO}_4$  upon  $\text{KNO}_3$ , in presence of hot  $\text{H}_2\text{SO}_4$ ; or of  $\text{FeCl}_2$  and  $\text{HCl}$ . (3) By passing  $\text{NH}_3$  over hot  $\text{MnO}_2$ .



**Properties.**—Condenses to a liquid at  $-11^\circ \text{C}$ ., under a pressure of 104, and at  $8^\circ \text{C}$ ., under a pressure of 270 atmospheres (CAILLETET, 1877). A colorless gas, having a disagreeable odor; destroying life if respired, even for a few seconds. It immediately oxidizes to  $\text{NO}_2$  when it comes in contact with the air. Solution of  $\text{FeSO}_4$  absorbs it freely, forming  $(\text{FeSO}_4)_2\text{NO}$ , from which compound the  $\text{NO}$  is driven off unchanged by boiling; see test for  $\text{HNO}_3$  (724). It is absorbed by nitric acid, forming a red, green, or blue solution, according to the temperature and degree of dilution.

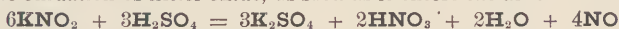
NITROUS ACID.  $\text{HNO}_2$ .Oxidation valence..... $\text{H}'\text{N}'''\text{O}''_2$ Structural valence.....  $\text{H}-\text{O}-\text{N}=\text{O}$ 

708. Nitrous anhydride ( $\text{N}_2\text{O}_3$ ). When starch, sugar, arsenious acid, and other easily oxidizable bodies are heated together with nitric acid, red

fumes are given off, consisting of varying quantities of  $\text{N}_2\text{O}_3$  and  $\text{NO}_2$ , and capable of being condensed to a very volatile green-colored liquid. This liquid may be employed for the purpose of preparing pure nitrous anhydride by passing a current of nitric oxide gas into the warmed liquid, and allowing the gas which is evolved to pass through a heated glass tube, the product being condensed in a tube plunged into a freezing mixture (HASSENBACH, *Jour. Prac. Chem.* (2), 4, 1). Nitrous anhydride is also obtained when a mixture of one volume of oxygen and four volumes of nitric oxide is allowed to pass through a hot tube; thus:  $2\text{NO} + \text{O} = \text{N}_2\text{O}_3$ . It is a deep-red gas. It condenses to a blue liquid at  $14.4^\circ \text{C}$ . under 755 m.m. pressure (GAINS, 1883, *Chem. News*, 48, 97).

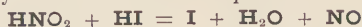
**Nitrous acid.**—Water at  $0^\circ \text{C}$ . dissolves  $\text{N}_2\text{O}_3$ , forming a blue solution, supposed to be nitrous acid ( $\text{HNO}_2$ ). But it has never been isolated. It decomposes at ordinary temperatures, thus:  $3\text{HNO}_2 = \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$ .

709. Likewise, when a metallic nitrite is transposed by dilute sulphuric acid, *nitric oxide* is evolved and *nitric acid* is left in solution; the brown gas which appears being formed by the oxidation of nitric oxide, as soon as it enters the air:

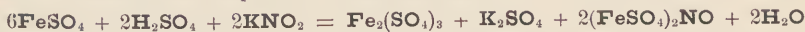


Nitrites, in many relations, act very readily as *oxidizing agents*; in other relations, with equal readiness, as *deoxidizing agents*. In both of these directions, they furnish reactions for their identification.

By **Oxidizing Action**, nitrites mostly furnish one-fourth of their oxygen, leaving nitric oxide. When decomposed in dilute cold solution by acetic acid or very dilute sulphuric acid, they instantly liberate *iodine* from iodides (*distinction from nitrates*, which do not give this reaction, even in concentrated solutions). Only a drop or two of the potassium iodide solution should be added; if but traces of nitrite are present, the iodine may be detected by starch or carbon disulphide.



710. Nitrites **with very dilute acids**—and with **acetic acid**—form *the brown liquid* with cold solutions of ferrous salts (*distinction from nitrates*, provided the reagent,  $\text{FeSO}_4$ , contains no free sulphuric or other free acid).



Nitrites, with **iodic acid**, or iodate and slight acidulation, give *free iodine*—a good distinction from nitrates.

A concentrated solution of nitrites, treated with a drop or two of **aniline** sulphate solution, gives the vapor of phenol, recognized by its odor ( $\text{C}_6\text{H}_7\text{N}$  oxidized to  $\text{C}_6\text{H}_6\text{O}$ )—a distinction from nitric acid. **Indigo** solution in sulphuric acid is bleached by nitrites.

As a **reducing agent**, a nitrite decolors **potassium permanganate** solution acidulated with sulphuric acid—an easy distinction from nitrate.

711. Nitrites are **all soluble in water**—*argentic nitrite* being but very sparingly soluble, and nitrites generally requiring for solution a larger proportion of water than nitrates. In solutions not very dilute, **silver nitrate** precipitates *silver nitrite*,  $\text{AgNO}_2$ , white. In moderately concentrated solutions of potassium nitrite, **cobalt nitrate** precipitates *potassio cobaltic nitrite*,  $(\text{KNO}_2)_6\text{Co}_2\text{O}_3(\text{N}_2\text{O}_3)_2$ , reddish-yellow, sparingly soluble in water (270).

In **analysis**, nitrites respond to the common test for nitrates (724); from which they are distinguished as stated in 709 to 711.

By ignition, metallic nitrites are resolved into *metallic oxides, nitrogen, and oxygen*; except silver and mercury nitrites, and the nitrites of some of the rarer metals which, like their oxides, are reduced to the metallic state by heat alone. Ammonium nitrite is decomposed into nitrogen and water. Heated with oxidizable bodies, nitrites deflagrate or detonate, like nitrates.

If cyanide of potassium be added to an alkaline nitrite, then some neutral solution of cobaltous chloride and a little acetic acid, the liquid becomes of a rosy-orange color from the formation of nitrocyanide of cobalt and potassium (C. D. BRAUN).

**712. Production of nitrites.**—The nitrites are all soluble; the silver and lead salts sparingly.

Nitrite of potassium may be made by fusion from the nitrate, oxygen being evolved, or by passing peroxide of nitrogen,  $\text{N}_2\text{O}_4$ , into potassium hydrate. Silver nitrite can be made from this by precipitation, and purified by recrystallization.

Basic lead nitrite can be made by boiling lead nitrate with metallic lead. The other nitrites are made by transposition; adding to silver nitrite, the chloride of the metal, which we wish to change to a nitrite, care being taken to add just enough. The nitrites of mercurous, tin, antimony, bismuth, aluminium, iron, and chromium have not been made.

**713. Oxidation.**—Nitrous acid acts sometimes as an oxidizing and sometimes as a reducing agent. When it oxidizes nitric oxide is formed. When it reduces nitric acid is produced.

$\text{H}_3\text{PO}_2$  *b.* Nitric oxide and phosphoric acid are formed.

$\text{H}_2\text{S}$  *c.* Hydrosulphuric acid has no action upon nitrite of potassium, but on addition of acetic acid sulphur separates, and if the solution is hot nitric oxide is formed, the fumes of peroxide of nitrogen being clearly visible.

$\text{H}_2\text{SO}_3$  *d.* Forms sulphuric acid and nitric oxide [*Gmelin-Kraut, Handbuch der Chemie*, I. 2, 458].

$\text{HClO}_3$  *g.* First forms peroxide of chlorine,  $\text{Cl}_2\text{O}_4$  [*Millon*], then hydrochloric acid [*Toussaint; Gmelin-Kraut, Handbuch der Chemie*, I. 2, 458].

$\text{Br}$  *h.* Free bromine seems to have no action on nitrous acid.

$\text{HI}$  *j.* Forms iodine and nitric oxide.

$\text{HIO}_3$  *k.* Forms iodine and nitric acid.

$\text{HCNS}$  *l.* Forms sulphuric and hydrocyanic acids, and nitric oxide. Sometimes traces of other cyanogen products are formed.

$\text{H}_4\text{Fe}(\text{CN})_6$  *m.* Forms first, ferricyanic acid, then nitroferricyanic acid.

$\text{H}_6\text{Fe}_2(\text{CN})_{12}$  *n.* Forms nitroferricyanic acid.

$\text{PbO}_2$  *o.* Forms  $\text{Pb}''$  and nitric acid [*Gmelin-Kraut, Handbuch der Chemie*, I. 2, 458].



**Hg'** *p.* Becomes **Hg°** [*Watts' Dictionary*, 4, 70 ; *Wurtz's Dictionnaire de Chimie*, I. 489 ; *Gmelin-Kraut, Handbuch der Chemie*, I. 2, 460].

Mercuric salts are not reduced [*Heppe, Chemische Reactionen*, 336].

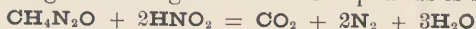
**Mn''** + *n r.* Forms **Mn''** and nitric acid.

**Co''** *s.* Changes **Co''** to **Co'''** (270) [*Watts' Dictionary*, I. 1045].

**Ni'''** *t.* Nitrites acidulated with phosphoric acid reduce **Ni'''** to **Ni''**, even in the cold.

**Cr<sup>vi</sup>** *u.* Becomes (**Cr<sub>2</sub>**)<sup>vi</sup> [*Watts' Dictionary*, 4, 70].

**Urea** *v.* On warming the nitrogen of both compounds is set free.



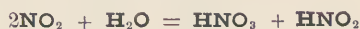
### NITROGEN PEROXIDE. **NO<sub>2</sub>**.

Oxidation valence.....**N<sup>iv</sup>O<sup>-''</sup><sub>2</sub>**

**714.** Vapor density at 140° C. (**H**=1) is 23 (DEVILLE and TROOST), showing that at that temperature the molecule is **NO<sub>2</sub>**. At 60.2° C. the density seems to indicate that the gas is made up of a mixture of equal parts of **NO<sub>2</sub>** and **N<sub>2</sub>O<sub>4</sub>**.

**Production.**—(1) By submitting one volume of oxygen and two parts of **NO** to a freezing mixture, **NO** + **O** = **NO<sub>2</sub>**. (2) By ignition of **Pb(NO<sub>3</sub>)<sub>2</sub>**. **2Pb(NO<sub>3</sub>)<sub>2</sub> = 2PbO + 4NO<sub>2</sub> + O<sub>2</sub>**. The **NO<sub>2</sub>** is separated from the oxygen by passing the mixed gases through a freezing mixture. (3) By adding oxygen to the oxides evolved by the action of nitric acid on metals and other reducing agents. It is formed when **NO** comes in contact with the air.

**Properties.**—A brownish-red gas, very irritating and poisonous when inhaled. Does not support ordinary combustion. It solidifies at -9° C. (PELIGOT) ; and boils at 21.6° C. (THORPE, 1880). At 0° C., water forms **HNO<sub>3</sub>** and **HNO<sub>2</sub>**. At higher temperatures, **HNO<sub>3</sub>** and **NO**. Potassium hydroxide forms a nitrate and a nitrite.



### NITRIC ACID. **HNO<sub>3</sub>**.

Oxidation valence.....**H<sup>i</sup>N<sup>v</sup>O<sup>-''</sup><sub>3</sub>**.

Structural valence.....**H-O-N<sup>o</sup>=O**

**715. Preparation of nitric anhydride, N<sub>2</sub>O<sub>5</sub>.**—(1) By passing dry chlorine over **AgNO<sub>3</sub>** at 93.5° C., condensing the gas in a cold receiver (DEVILLE). (2) By passing **NO<sub>2</sub>Cl** over **AgNO<sub>3</sub>** (ODET and VIGNON). (3) By treating **HNO<sub>3</sub>** with **P<sub>2</sub>O<sub>5</sub>** (WEBER).

1.  $4\text{AgNO}_3 + 2\text{Cl}_2 = 4\text{AgCl} + 2\text{N}_2\text{O}_5 + \text{O}_2$
2.  $\text{AgNO}_3 + \text{NO}_2\text{Cl} = \text{AgCl} + \text{N}_2\text{O}_5$
3.  $6\text{HNO}_3 + \text{P}_2\text{O}_5 = 2\text{H}_3\text{PO}_4 + 3\text{N}_2\text{O}_5$

A colorless solid, melting at  $30^\circ \text{C}$ ., and boiling at  $45^\circ$  to  $50^\circ \text{C}$ . (DEVILLE). It is instable, decomposed by heat above its boiling point. It unites with water to form the corresponding acid.

**716.** Absolute nitric acid— $\text{HN}^\vee\text{O}_3$ —is a colorless, transparent, mobile liquid, of the specific gravity of 1.58 at  $15^\circ \text{C}$ . [Millon], boiling at  $86^\circ \text{C}$ . ( $187^\circ \text{F}$ .) with partial decomposition, leaving nitric acid mixed with water. Aqueous nitric acid having 70 per cent. of  $\text{HNO}_3$ , and corresponding to  $(\text{HNO}_3)_2(\text{H}_2\text{O})_3$ , specific gravity 1.42, appears to be a definite hydrate, as both stronger and weaker acids are, by boiling, reduced to this composition, which boils at  $123^\circ \text{C}$ . ( $253^\circ \text{F}$ .) The reagent designated in this work as *nitric acid* has a specific gravity of 1.2, and about 35 per cent. of  $\text{HNO}_3$  (Fresenius' standard).

**717.** By heating, by action of the light, and by organic particles from the air, strong nitric acid parts with oxygen and generates nitrous anhydride and nitric peroxide,  $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$ , which remain dissolved with a yellow color. The tendency to this change is very strong in absolute nitric acid, which cannot well be preserved colorless; and the acid of 70 per cent. colors far more readily than that of 35 per cent. The nitrogen oxides may be expelled by boiling; or, with less waste of nitric acid, by passing pure air through it, by means of a bellows, a wash-bottle, and, to avoid dilution, a drying-tube.

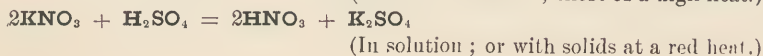
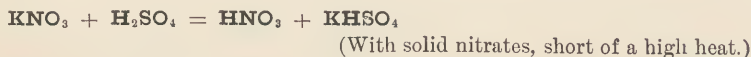
Nitric acid is a *strong oxidizing agent*, and, as such, its reactions with oxidizable elements and compounds are in constant requisition in analysis. Unless heated, nitric acid does not generally oxidize substances as quickly as chlorine with water.

**718.** In *oxidizing* and dissolving **metals** or **metalloids**, and in oxidizing **lower oxides**, nitric acid most frequently disengages water and nitric oxide (*d*); but, with certain substances and under certain conditions, other residues are chiefly produced, as dinitrogen tetroxide (*b*), nitrous acid (*c*), nitrous oxide (*e*), nitrogen (*f*), hydrogen (*a*), ammonium nitrate (*g*). Examples of several of these results, as varied by conditions, are seen in the case of zinc (290 *c, d, e*), iron (202 *b, c, d, e*), tin (526 *d, e*), arsenious acid (475 *c*). Further, in the study of oxidations, see 733.

- a.*  $\text{HNC}_3 = \text{NO}_2$  (combined) + **H**
- b.*  $2\text{HNO}_3 = \text{O}$                    “                   +  $\text{H}_2\text{O} + \text{N}_2\text{O}_4$
- c.*  $\text{HNO}_3 = \text{O}$                    “                   +  $\text{HNO}_2(2\text{HNO}_2 = \text{H}_2\text{O} \text{ and } \text{N}_2\text{O}_3)$
- d.*  $2\text{HNO}_3 = 3\text{O}$                    “                   +  $\text{H}_2\text{O} + 2\text{NO}$
- e.*  $2\text{HNO}_3 = 4\text{O}$                    “                   +  $\text{H}_2\text{O} + \text{N}_2\text{O}$
- f.*  $2\text{HNO}_3 = 5\text{O}$                    “                   +  $\text{H}_2\text{O} + 2\text{N}$  (combined).
- g.*  $10\text{HNO}_3 = 8\text{NO}_3$            “                   +  $3\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$

**719.** The metallic sulphides (except mercuric sulphide) dissolve as nitrates by action of nitric acid, more or less readily; the *sulphur* being at first mostly left as a residue. But as fast as the sulphur is oxidized, metallic *sulphates* are formed, soluble or insoluble (equations in 388).

**720.** Nitric acid is formed by transposition between sulphuric acid and nitrates:

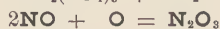
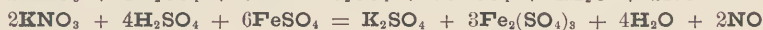
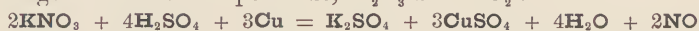


**721.** The **Nitrates** are all soluble in water. There are a few *basic* nitrates—basic bismuth nitrate, basic mercurous and mercuric nitrates—insoluble in water. Many of the nitrates are insoluble in alcohol.

Most of the tests for the **identification** of nitric acid are made by its deoxidation, disengaging a lower oxide of nitrogen (724), or even, by complete deoxidation, forming ammonia (726).

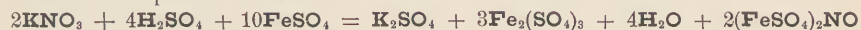
**722.** **Sulphuric acid** is transposed with metallic nitrates, with but little decomposition of the nitric acid formed (720). The colorless or slightly reddish gas does not rise till the mixture is very hot—absolute nitric acid not being, like hydrochloric acid, a gas at ordinary temperatures. It reddens litmus, and has a characteristic acid odor.

**723.** If, with the sulphuric acid, a bit of **copper** turning, or a crystal of ferrous sulphate, is added to a concentrated solution or residue of nitrate, the mixture gives off abundant brown vapors; the colorless *nitric oxide*, **NO**, which is set free from the mixture, oxidizing immediately in the air to dinitrogen trioxide and peroxide, **N<sub>2</sub>O<sub>3</sub>** and **NO<sub>2</sub>** :



The *three atoms of oxygen furnished by two molecules of nitrate* (as in 718 *d*), suffice to oxidize three atoms of copper; so that **3CuO** with **3H<sub>2</sub>SO<sub>4</sub>**, may form **3CuSO<sub>4</sub>** and **3H<sub>2</sub>O**. The same three atoms of oxygen (having six bonds) suffice to oxidize six molecules of ferrous salt into three molecules of ferric salt; so that **6FeSO<sub>4</sub>** with **3H<sub>2</sub>SO<sub>4</sub>**, can form **3Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>**, and **3H<sub>2</sub>O**.

**724.** Now if, by the last-named reaction, the nitric oxide is disengaged in cold solution, with excess of ferrous salt and of sulphuric acid, instead of passing off, the nitric oxide combines with the ferrous salt, forming a *black brown liquid*, **(FeSO<sub>4</sub>)<sub>2</sub>NO**, decomposed by heat and otherwise unstable. And **2NO** require **4FeSO<sub>4</sub>**, in addition to the proportion of ferrous salt in the equation in 723.



This exceedingly delicate test for nitric acid or nitrates in solution may be conducted as follows: Take sulphuric acid to a quarter of an inch in depth in the test-tube; add without shaking a nearly equal bulk of solution of ferrous sulphate, and cool the liquid; then add slowly of the solution to be tested for nitric acid, slightly tapping the test-tube on the side, but not shaking it. The "*brown ring*" forms, between the two layers of liquid—violet, red, brown, or black, according to proportions and conditions. The color disappears on heating, with evolution of nitrous gas, yellowish ferric solution remaining. The test is somewhat more delicate if a crystal of ferrons sulphate be added, instead of the solution, and the test-tube be set aside for several hours.

**725.** Slight traces of nitrate (as in rain or river-waters) are detected, according to the above reaction, by first reducing to nitrite by heating for some time with **zinc amalgam**, or less readily with finely divided **zinc**. *Nitrites previously found to be absent*, by the same test, viz.: To a thick layer of the clear filtered water the solution of ferrous sulphate is added, and the brown coloration obtained, if nitrites have been formed. Or, a drop or two of **potassium iodide** solution with fresh **starch-paste**, and a drop or two of very dilute sulphuric acid, is added (709).

The reduction to nitrite may also be effected by **zinc** or **cadmium**, in acidulated solution, as follows (STORER):\* Boil the solution, slightly acidulated (by addition of sulphuric acid, if necessary) with metallic cadmium (or zinc), for about five minutes, in a tall vessel—or, better, in a retort with raised condenser—and filter or decant from the metal. Then add a mixture of potassium iodide and starch-paste—or, better, a mixture of zinc iodide, zinc chloride, and starch-paste. The iodine-color indicates nitrous acid, reduced from nitric acid. Without the boiling in acidulate solution, hydrogen peroxide may be formed, giving a fallacious indication for nitric acid.

**726. Reduction to Ammonia**, by strong reducing agents (718 g), is a valuable resource in identifying nitric acid. The tests based on this principle are delicate, but do not distinguish nitric acid from nitrous acid or cyanogen compounds. Ammonia, if found already present, may be distilled off. In those tests requiring use of strong alkali, nitrogenous organic substances will give ammonia. The ammonia obtained is, in most methods, identified by **potassium mercuric iodide**—a reaction so delicate as to show the frequent presence of ammonia in distilled water and many reagents. Hence, all these must be first tested, if necessary, after distillation. Larger quantities of ammonia are recognized in vapor, by litmus, etc.

In neutral solutions, **sodium amalgam** is used as follows—a method for the total of nitric and nitrous acids and ammonia, in potable waters, and otherwise applied: To 6 or 8 cub. cent. ( $1\frac{1}{2}$  or 2 fluid drachms) of the solution (in a carefully cleaned test-tube) add 100 to 200 grains of sodium-amalgam which is  $\frac{1}{2}$  per cent. sodium; cork the tube lightly and leave for twelve hours. Hydrogen is always slowly evolved, and escapes. Decant and rinse into a glass cylinder one inch wide, and at least six inches high, and add water to about 60 cub. cent. (2 fluid ounces). Nessler's test solution is now applied. The test cannot be made before decantation from the amalgam, as the nascent hydrogen interferes.

The *nascent hydrogen* developed by dissolving **zinc** in solution of **potassium hydroxide** also reduces nitrates in the alkaline solution, and *evolves ammonia*. This is a convenient and efficient test by reduction to ammonia. The solution should be strongly charged with potassium hydrate, the zinc finely divided, and mixed with half its weight of **iron** filings. The mixture is then *distilled* at a boiling rate, and the distillate tested for ammonia by potassium mercuric iodide. The reagents, including the water, should be first tested in the apparatus.

**Metallic magnesium** may be used for the reduction, as follows: Acidulate with phosphoric acid; add magnesium wire, and leave, cold, a few minutes. Then test for ammonia, by the potassium mercuric iodide solution with potassium hydroxide. If interfering acids are present, add potassium hydroxide, distill, and test the distillate for ammonia.

**Stannous chloride and hydrochloric acid**, heated with a nitrate, form stannic chloride, and convert nitric acid to *ammonia* (which remains as ammonium salt).

**727.** With **hydrochloric acid**, nitric acid forms free chlorine, etc. (nitrohydrochloric acid), applied as a test for nitric acid—in absence of other oxidizing agents—as follows: Heat a little hydrochloric acid in a test-tube to boiling; color it (slightly) with a drop or

\* *Amer. Jour. Science*, [3] XII. 176 (Sept., 1876).



two of very dilute **indigo solution** (in sulphuric acid), and boil again. If the hydrochloric acid was pure, the color remains unchanged. The addition of a nitrate, with boiling, now quickly bleaches the solution.

**728. Phenol**,  $\text{C}_6\text{H}_5\text{OH}$ , gives a deep red-brown color with nitric acid, by formation of nitrophenol (mono, di, or tri),  $\text{C}_6\text{H}_4(\text{NO}_2)\text{OH}$  to  $\text{C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$ , "picric acid" or nitrophenic acid. A mixture of one part of phenol (cryst. carbolic acid), four parts of strong sulphuric acid, and two parts of water, constitutes a reagent for a very delicate test for nitrates (or nitrites), a few drops being sufficient. With unmixed nitrates, the action is explosive, unless upon very small quantities. The addition of potassium hydroxide deepens and brightens the color of the nitrophenic acid solution.

**729. Brucia**, dissolved in concentrated sulphuric acid, treated (on a porcelain surface) with even traces of nitrates, gives a fine deep-red color, soon paling to reddish-yellow. If now stannous chloride dilute solution be added, a fine red-violet color appears. (Chloric acid gives the same reaction) **Aniline Sulphate** solution, with a half volume of concentrated sulphuric acid, treated (on a porcelain surface) with traces of nitrates, gives a rose-red color, commencing with red lines, and when concentrated appearing brown-red.

**730.** By slight **ignition**, nitrates of the fixed alkali and alkaline earth metals are reduced to *nitrites*, recognized as shown in 709. Stronger ignition changes them to *caustic bases*, with formation of brown vapors. Nitrates of heavy metals are mostly changed to *oxides* by heat; ammonium nitrate, wholly to *nitrous oxide* and water.

**Heated on Charcoal**, or with potassium cyanide, or sugar, sulphur, or other easily oxidizable substance (as in gunpowder), nitrates are reduced with *deflagration* or *explosion*, more or less violent. With potassium cyanide, on platinum foil, the deflagration is especially vivid. In this reaction free *nitrogen* is evolved, as by equation *f*, 718.

Strongly heated with excess of potassium hydrate and sugar or other carbonaceous compound, in a dry mixture, nitrates are reduced to *ammonia*, which is evolved, and may be detected. In this carbonaceous mixture, the nitrogen of nitrates reacts with alkalis, like the unoxidized nitrogen in carbonaceous compounds (compare 705, 718 *g*, and 726)

**731. Free Nitric Acid** may be distinguished from nitrates, by giving the *brown liquid* with ferrous salt, on reduction by zinc, *without addition of sulphuric acid*, as stated in 725, and by *coloring quill-cuttings* or white woollen fabrics yellow when the solution is evaporated with them on the water-bath. The yellow color substance contains xanthoproteic acid, and is formed by action of nitric acid upon any gelatinoid substance—as the skin—and upon ordinary albumenoid substances.

**732.** Nitrates are all soluble. *a.* They are formed by the action of nitric acid upon metals, as described in 733. *b.* By dissolving the oxides, hydroxides, or carbonates of the metals in nitric acid. Mercurous, stannous, manganous, and ferrous nitrates should not be evaporated to expel excess of nitric acid, since a higher metallic form would result. The crystals may be washed in cold water, to free them from the uncombined acid. All nitrates are decomposed by heat; a few, the alkalis and alkaline earths, first evolve oxygen and form nitrites, afterward a mixture of oxygen and nitrogen, leaving the oxides; others either free nitric acid or a mixture of the oxides of nitrogen, until only the oxide of the metal remains. There are two exceptions, silver and mercury, in which cases only the free metals remain.

**733.** Of course nitric acid can never act as a reducing agent. Acting as an oxidizing agent, it may form  $\text{NH}_3$ ,  $\text{N}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}_3$ , or  $\text{N}_2\text{O}_4$ .

If the nitric acid is in excess, and a boiling heat be used, the product is nearly all  $\text{NO}$ , while excess of the reducing agent and a low temperature favor the formation of  $\text{NH}_3$ .

A convenient test for  $\text{NO}$  is made by passing the gas into ferrous sulphate. (See 718 and *Acworth and Armstrong, Jour. Chem. Society*, 32, 54.)

The action upon  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{HCNS}$  has been given (659, 702).

$\text{H}_3\text{PO}_2$  *b.* Becomes phosphoric acid.

$\text{H}_2\text{S}$  *c.* Forms sulphur, and may be further oxidized to sulphuric acid. The nitric acid must be stronger than sp. gr. 1.18 [*Gmelin-Kraut, Handbuch*, 1. 2, 219].

$\text{H}_2\text{SO}_3$  *d.* Becomes sulphuric acid.

$\text{HCl}$  *e.* Forms nitrohydrochloric acid.

$\text{HClO}_3$  *f.* Nitric acid added to a chlorate liberates chloric acid, which decomposes, but the nitric is not changed [*Penny, Jour. Prakt. Chem.*, 23, 296].

$\text{HBr}$  *g.* Gives free bromine.

$\text{I}$  *h.* Forms iodic acid; action slow, and strong nitric acid should be used—at least sp. gr. 1.42. This is a practical method for making iodic acid, if acid of sp. gr. 1.48 is used [*Bousson, Comptes Rendus Academie des Sciences*, 13, 1111].

$\text{HI}$  *i.* Forms first free iodine, then iodic acid.

$\text{HCNS}$  *j.* Forms hydrocyanic and sulphuric acids.

With strong nitric acid, traces of carbonic acid are formed [*Vögel, Gmelin's Hand-book*, 8, 75].

$\text{H}_4\text{Fe}(\text{CN})_6$  *k.* Forms ferriecyanic acid [*Watts' Dictionary*, 2, 250], and then nitroferriecyanic acid.

$\text{H}_6\text{Fe}_2(\text{CN})_{12}$  *l.* Forms nitroferriecyanic acid.

*m.* Nitric acid oxidizes all ordinary metals. (It does not act upon gold or platinum.) It forms nitrates, except in the case of tin, antimony, and arsenic, with which it forms  $\text{H}_{10}\text{Sn}_5\text{O}_{15}$ ,  $\text{Sb}_2\text{O}_5$ , and  $\text{H}_3\text{AsO}_4$ .

With the respective metals it forms  $\text{Hg}'$  or  $\text{Hg}''$ ,  $\text{Sn}''$  or  $\text{Sn}'''$ ,  $\text{As}''$  or  $\text{As}^v$ ,  $\text{Sb}'''$  or  $\text{Sb}^v$ ,  $\text{Fe}''$  or  $\text{Fe}'''$ , according to the amount of nitric acid employed.

With copper it forms cupric nitrate (never cuprous); with cobalt it forms cobaltous nitrate.

$\text{Pb}_3\text{O}_4$  *n.* Becomes plumbic nitrate and  $\text{PbO}_2$ . The nitric acid is not reduced.

$\text{Hg}'$  *o.* Becomes  $\text{Hg}''$ .

$\text{SnO}$  *p.* Becomes  $\text{SnO}_2$ . (Not stannic nitrate.)

- $\text{H}_3\text{AsO}_3$  *q*. Becomes  $\text{H}_3\text{AsO}_4$ .  
 $\text{Sb}_2\text{O}_3$  *r*. Becomes  $\text{Sb}_2\text{O}_5$ .  
 $\text{Cu}'$  *s*. Becomes  $\text{Cu}''$ .  
*t*.  $\text{MnO}$ ,  $\text{NiO}$ ,  $\text{CoO}$ ,  $\text{Cr}_2\text{O}_3$  are not oxidized.  
 $\text{Fe}''$  *u*. Becomes  $\text{Fe}'''$ .

OXYGEN.  $\text{O} = 15.9633$ .

**734.** The vapor density ( $\text{H} = 1$ ), 16, shows that the molecule of oxygen has two atoms.

**Occurrence.**—The rocks, clay, and sand constituting the main part of the earth's crust contain from 44 to 48 per cent. of oxygen; and as water contains 88.87 per cent., it has been estimated that one-half of the crust is oxygen. Except in atmospheric air, it is always found combined.

**Preparation.**—(1) By igniting  $\text{HgO}$ . (2) By heating  $\text{KClO}_3$  to  $350^\circ \text{C}$ .,  $\text{KClO}_4$  is produced and oxygen is evolved; at a higher temperature the  $\text{KClO}_4$  becoming  $\text{KCl}$ . But in presence of  $\text{MnO}_2$  the chlorate is completely changed to  $\text{KCl}$  at  $200^\circ \text{C}$ ., without forming  $\text{KClO}_4$ , the  $\text{MnO}_2$  not being changed. Spongy platinum may be substituted for  $\text{MnO}_2$ . (3) Action of heat on similar salts furnishes oxygen—*e.g.*,  $\text{KClO}$  and  $\text{KClO}_2$  forming  $\text{KCl}$ ,  $\text{KBrO}_3$  forming  $\text{KBr}$ ,  $\text{KIO}_3$  and  $\text{KIO}_4$  forming  $\text{KI}$ ,  $\text{KNO}_3$  forming  $\text{KNO}_2$  (at a white heat forming  $\text{K}_2\text{O}$ ,  $\text{NO}$ , and  $\text{O}$ ). (4) By action of heat on metallic oxides, as shown in the equations below. (5)  $\text{BaO}$ , heated in the air to  $550^\circ \text{C}$ ., becomes  $\text{BaO}_2$ , and at  $800^\circ \text{C}$ . is resolved into  $\text{BaO}$  and free oxygen, making *theoretically* a cheap process. (6) By heating higher oxides or their salts with  $\text{H}_2\text{SO}_4$ :  $\text{Cr}^{\text{vi}}$  is changed to  $(\text{Cr}_2)^{\text{vi}}$ ,  $(\text{Co}_2)^{\text{vi}}$  to  $\text{Co}''$ ,  $(\text{Ni}_2)^{\text{vi}}$  to  $\text{Ni}''$ ,  $\text{Bi}^{\text{iv}}$  to  $\text{Bi}'''$ ,  $\text{Fe}^{\text{vi}}$  to  $(\text{Fe}_2)^{\text{vi}}$ ,  $\text{Pb}^{\text{iv}}$  to  $\text{Pb}''$ ,  $\text{Mn}'' + n$  to  $\text{Mn}''$ ; in each case a sulphate is formed and oxygen given off. (7) By passing sulphuric acid over red hot bricks; the  $\text{SO}_2$  is separated by water, and after conversion into  $\text{H}_2\text{SO}_4$  is used over again. (8) The following *cheap process* is now employed on a *large scale*. Steam is passed over sodium manganate at a dull red heat;  $\text{Mn}_2\text{O}_3$  and oxygen are formed. Then, without change of apparatus or temperature, air instead of steam is passed over the mixture of  $\text{Mn}_2\text{O}_3$  and  $\text{NaOH}$ . The  $\text{Mn}_2\text{O}_3$  is thus again oxidized to  $\text{Na}_2\text{MnO}_4$ , and free nitrogen is liberated.

1.  $2\text{HgO}$  (at  $500^\circ \text{C}$ ) =  $2\text{Hg} + \text{O}_2$
2. *a.*  $2\text{KClO}_3$  (at  $350^\circ \text{C}$ .) =  $\text{KClO}_4 + \text{KCl} + \text{O}_2$   
*b.*  $2\text{KClO}_3$  (at red heat) =  $2\text{KCl} + 3\text{O}_2$   
*c.*  $2\text{KClO}_3 + n\text{MnO}_2$  (at  $200^\circ \text{C}$ .) =  $n\text{MnO}_2 + 2\text{KCl} + 3\text{O}_2$
3. *a.*  $\text{KClO}_2$  + ignition =  $\text{KCl} + \text{O}_2$   
*b.*  $2\text{KBrO}_3$  + " =  $2\text{KBr} + 3\text{O}_2$   
*c.*  $2\text{KIO}_3$  + " =  $2\text{KI} + 3\text{O}_2$   
*d.*  $\text{KIO}_4$  + " =  $\text{KI} + 2\text{O}_2$   
*e.*  $2\text{KNO}_3$  + " =  $2\text{KNO}_2 + \text{O}_2$

- f.  $4\text{KNO}_2$  (white heat) =  $2\text{K}_2\text{O} + 4\text{NO} + \text{O}_2$
4. a.  $2\text{Pb}_2\text{O}_4$  " =  $6\text{PbO} + \text{O}_2$
- b.  $2\text{Sb}_2\text{O}_5$  (red heat) =  $2\text{Sb}_2\text{O}_4 + \text{O}_2$
- c.  $\text{Bi}_2\text{O}_5$  " =  $\text{Bi}_2\text{O}_3 + \text{O}_2$
- d.  $4\text{CrO}_3$  (about  $200^\circ \text{C}$ ) =  $2\text{Cr}_2\text{O}_3 + 3\text{O}_2$
- e.  $4\text{K}_2\text{Cr}_2\text{O}_7$  (red heat) =  $2\text{Cr}_2\text{O}_3 + 4\text{K}_2\text{CrO}_4 + 3\text{O}_2$
- f.  $6\text{Fe}_2\text{O}_3$  (white heat) =  $4\text{Fe}_3\text{O}_4 + \text{O}_2$
- g.  $3\text{MnO}_2$  " =  $\text{Mn}_3\text{O}_4 + \text{O}_2$
- h.  $6\text{Co}_2\text{O}_3$  (dull red heat) =  $4\text{Co}_3\text{O}_4 + \text{O}_2$
- i.  $2\text{Ni}_2\text{O}_3$  " " =  $4\text{NiO} + \text{O}_2$
- j.  $2\text{Ag}_2\text{O}$  ( $300^\circ \text{C}$ .) =  $4\text{Ag} + \text{O}_2$
5.  $2\text{BaO}_2$  ( $800^\circ \text{C}$ .) =  $2\text{BaO} + \text{O}_2$
6.  $2\text{K}_2\text{Cr}_2\text{O}_7 + 8\text{H}_2\text{SO}_4 = 2\text{K}_2\text{Cr}_2(\text{SO}_4)_4 + 3\text{O}_2 + 8\text{H}_2\text{O}$   
 $2\text{K}_2\text{Mn}_2\text{O}_8 + 6\text{H}_2\text{SO}_4 = 2\text{K}_2\text{SO}_4 + 4\text{MnSO}_4 + 5\text{O}_2 + 6\text{H}_2\text{O}$   
 $2\text{Pb}_2\text{O}_4 + 6\text{H}_2\text{SO}_4 = 6\text{PbSO}_4 + 6\text{H}_2\text{O} + \text{O}_2$
7.  $2\text{H}_2\text{SO}_4$  (upon red hot bricks) =  $2\text{SO}_2 + 2\text{H}_2\text{O} + \text{O}_2$
8.  $4\text{Na}_2\text{MnO}_4 + 4\text{H}_2\text{O}$  (dull red heat) =  $8\text{NaOH} + 2\text{Mn}_2\text{O}_3 + 3\text{O}_2$   
 $8\text{NaOH} + 2\text{Mn}_2\text{O}_3 + \text{air}, 3(\text{O}_2 + 4\text{N}_2) = 4\text{Na}_2\text{MnO}_4 + 4\text{H}_2\text{O} + 12\text{N}_2$

**735. Properties.**—By pressure and cold it is condensed to a colorless liquid. This liquid boils under ordinary atmospheric pressure at  $-184^\circ \text{C}$ .; and under a pressure of 50 atmospheres at  $-113^\circ \text{C}$ . (WROBLEWSKI, 1884, *Compt. Rend.* 98, 982). Pure oxygen may be breathed for a short time without injury. A rabbit placed in pure oxygen at  $24^\circ \text{C}$ . ( $75^\circ \text{F}$ .) lived for three weeks, eating voraciously all the time, but nevertheless becoming thin. The action of oxygen at  $7.2^\circ \text{C}$ . ( $45^\circ \text{F}$ .) is to produce narcotism and eventually death. When oxygen is cooled by a freezing mixture it induces so intense a narcotism that operations may be performed under its influence. Compressed oxygen is "the most fearful poison known." The pure gas at a pressure of 3.5 atmospheres, or air at a pressure of 22 atmospheres, produces violent convulsions, simulating those of strychnia poisoning, ultimately causing death. The arterial blood in these cases is found to contain about twice the quantity of its normal oxygen. Further, compressed oxygen stops fermentation, and permanently destroys the power of yeast (PAUL BERT).

At varying temperatures oxygen combines directly with all metals except silver, gold, and platinum, and with these it may be made to combine by precipitation. It combines with all non-metals except fluorine; the combination occurring directly, at high temperatures, except with **Cl**, **Br**, and **I**, which require the intervention of a third body.

### OZONE. $\text{O}_3$ (?).

**736.** Ozone is the name of a modified form of oxygen, of the true nature of which there is still some doubt, as it has never been obtained free from ordinary oxygen. It is found in small quantities in the air, especially



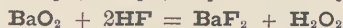
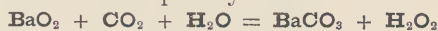
at the sea-shore and in the open country. It is never found in the atmosphere of crowded cities.

**Production**—(1) By the action of electricity on moist oxygen or air, better at a low temperature. (2) By the electrolysis of dilute sulphuric acid. (3) By the combustion of phosphorus in moist air. (4) Formed during the evaporation of water.

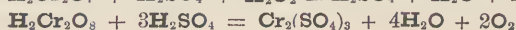
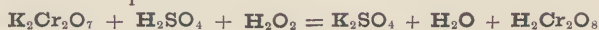
**Properties.**—When inhaled in small quantities, supposed to be healthful. In larger quantities irritates the eyes and nose. Has proved fatal to animals that have been made to breathe it. Condenses to a liquid at a higher temperature than ordinary oxygen. Theory represents the molecule as having three atoms,  $O_3$ , ordinary oxygen two atoms,  $O_2$ . When heated to  $300^\circ C$ . it is decomposed, forming ordinary oxygen, with an increase in volume; perhaps thus,  $2O_3 = 3O_2$ . It liberates iodine from  $KI$ , probably thus,  $2KI + H_2O + O_3 = 2KOH + I_2 + O_2$ . It is an energetic oxidizing agent, oxidizing where ordinary oxygen does not.

#### HYDROGEN PEROXIDE. $H_2O_2$ .

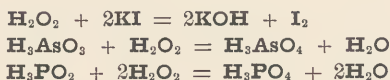
**737.** This remarkable substance is usually made by treating the peroxide of the alkalis or alkaline earths with dilute acids. Either the oxyacids or hydracids will answer; even carbonic will complete the result. It is generally manufactured by treating  $BaO_2$  with  $CO_2$ ,  $HCl$ ,  $H_2SO_4$ , or  $HFl$ ; on a large scale the latter is more frequently used.



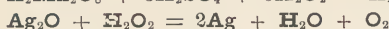
**Properties.**—The pure anhydrous  $H_2O_2$  is a transparent, colorless liquid, sp. gr. 1.4. Does not freeze at  $-30^\circ C$ . Volatilizes slowly in a vacuum without decomposition, if the temperature is not allowed to rise above  $15^\circ C$ ., otherwise explosion occurs. Does not redden but slowly bleaches litmus paper. Bleaches most organic colors, but more slowly than  $Cl$  or  $SO_2$ . It is odorless, and tastes bitter. The concentrated  $H_2O_2$ , placed upon the skin, soon produces a blister. It decomposes slowly, at a low temperature, rapidly at a high temperature, into oxygen and water. The dilute solution in water is more stable. It is soluble in ether, making solution more stable than in water. It may be removed from the aqueous solution by shaking with ether. The acidified aqueous solution is more stable than the neutral or the alkaline. The best test for  $H_2O_2$  is to add  $K_2Cr_2O_7$ , and a little dilute  $H_2SO_4$ . The chromium is oxidized to perchromic acid,  $H_2Cr_2O_8$ ; on adding ether and shaking, it is all absorbed by the ether, and, rising to the surface, is recognized by its intense blue color. Perchromic acid is instable in water, decomposing into oxygen and chromic salt. Its ethereal solution is permanent.



It generally oxidizes. Thus it changes  $\text{Pb}''$  to  $\text{Pb}^{\text{IV}}$ ,  $(\text{Hg}_2)''$  to  $\text{Hg}''$ ,  $\text{Sn}''$  to  $\text{Sn}^{\text{IV}}$ ,  $\text{As}'''$  to  $\text{As}^{\text{V}}$ ,  $\text{Bi}'''$  to  $\text{Bi}^{\text{V}}$ ,  $\text{H}_3\text{PO}_2$  to  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{S}$  to  $\text{S}$ ,  $\text{H}_2\text{SO}_3$  to  $\text{H}_2\text{SO}_4$ ,  $\text{HI}$  to  $\text{I}$ , etc.



Yet it sometimes strangely acts as a reducing agent; and when it does so, ordinary oxygen is evolved from both substances. It reduces  $\text{K}_2\text{Mn}_2\text{O}_8$  to a manganeous salt in acid mixture; but in alkaline mixture to  $\text{MnO}_2$ . It reduces gold, silver, and platinum from their oxides.



It is estimated volumetrically by measuring the oxygen evolved on adding  $\text{K}_2\text{Mn}_2\text{O}_8$ .

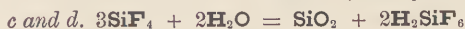
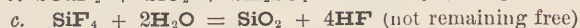
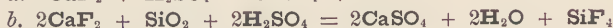
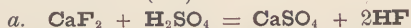
**Uses**—It has been used in medicine, externally as a lotion, and internally for diabetes and oxaluria. It constitutes the golden hair-dye of the shops, the dyeing being really a bleaching (oxidizing) action. It is also used for bleaching and cleaning oil paintings and stained engravings (converting  $\text{PbS}$  into  $\text{PbSO}_4$ ).

#### FLUORINE. $F = 18.984$ .

**738.** Since Davy's experiments in 1813, many others have attempted the isolation of fluorine. In his zeal the unfortunate Louyet fell a victim to the poisonous fumes which he inhaled. Faraday, Gore, Fremy, and others took up the problem in succession, but it was not ultimately solved until H. Moissan, in 1886, produced a gas which the chemical section of the French Academy of Sciences decided to be fluorine. Many ingenious experiments had been made in order to obtain fluorine in a separate state, but it was found that it invariably combined with some portion of the material of the vessel in which the operation was conducted. The most successful of the early attempts to isolate fluorine appears to have been made, at the suggestion of Davy, in a vessel of fluor-spar itself, which could not, of course, be supposed to be in any way affected by it. Moissan's method was as follows: The hydrofluoric acid having been very carefully obtained pure, a little potassium hydrofluoride was dissolved in it to improve its conducting power, and it was subjected to the action of the electric current in a U-tube of platinum, down the limbs of which the electrodes were inserted; the negative electrode was a rod of platinum, and the positive was made of an alloy of platinum with 10 per cent. of iridium. The U-tube was provided with stoppers of fluor-spar, and platinum delivery tubes for the gases, and was cooled to  $-23^\circ \text{C}$ . The gaseous fluorine, which was extricated at the positive electrode, was colorless, and possessed the properties of chlorine, but much more strongly marked. It decomposed water immediately,

seizing upon its hydrogen, and liberating oxygen in the ozonized condition; it exploded with hydrogen, even in the dark, and combined, with combustion, with most metals and non-metals, even with boron and silicon in their crystallized modifications. **As, Sb, S, I,** alcohol, ether, benzene, terebenthene, and petroleum took fire in the gas. Carbon was not attacked by it. (H. MOISSAN, 1886; *Compt. Rend.*, 103, 202, and 256; *Jour. Chem. Soc.*, 50, 849, and 976.)

**739. Fluorine**, in several characteristics, appears as the first member of the Chlorine Series of Elements. It cannot be preserved in the elemental state, as it combines with the materials of vessels (except fluor-spar), and instantly decomposes water, forming *hydrofluoric acid*, **HF**, an acid prepared by acting on calcium fluoride with sulphuric acid (*a*). Fluorine also combines with silicon as **SiF<sub>4</sub>**, *silicon fluoride*, a gaseous compound, prepared by acting on calcium fluoride and silicic anhydride with sulphuric acid (*b*). On passing silicon fluoride into water, a part of it is transposed with the water, forming silicic acid and hydrofluoric acid (*c*); but this hydrofluoric acid does not at all remain free, but combines with the other part of the fluoride of silicon, as *hydrofluosilicic acid*, (**HF**)<sub>2</sub>**SiF<sub>4</sub>**, or **H<sub>2</sub>SiF<sub>6</sub>** (*d*). This acid is used as a reagent; forming metallic silicofluorides, soluble and insoluble (742).



## HYDROFLUORIC ACID.

**740.** A colorless, intensely corrosive gas, soluble in water to a liquid that reddens litmus, rapidly corrodes glass, porcelain, and the metals, except platinum and gold (lead but slightly). Both the solution and its vapor act on the flesh as an insidious and virulent caustic, giving little warning, and causing obstinate ulcers. The anhydrous acid at 25° C. (77° F.) has a vapor density (**H** = 1) of 20, indicating that the molecule at this temperature is **H<sub>2</sub>F<sub>2</sub>**. But at 100° C. it is only 10, indicating that at that temperature the molecule is **HF**. The anhydrous liquid acid boils at 19.44° C. (GORE, 1869), and does not solidify at -34.5° C.

The **Fluorides** of the alkali metals are freely soluble in water, the solutions alkaline to litmus and slightly corrosive to glass; the fluorides of the alkaline earth metals are insoluble in water; of copper, lead, zinc, and ferrium, sparingly soluble; of silver and mercury readily soluble. Fluorides are identified by the action of the acid upon glass.

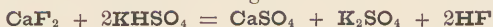
**Calcium chloride** solution forms, in solution of fluorides or of hydrofluoric acid, a gelatinous and transparent precipitate of *calcium fluoride*, **CaF<sub>2</sub>**, slightly soluble in cold hydrochloric or nitric acid and in ammonium chloride solution. **Barium chloride** precipitates, from free hydrofluoric acid less perfectly than from fluorides, the voluminous, white, *barium fluoride*, **BaF<sub>2</sub>**. Silver nitrate gives no precipitate.

**Sulphuric acid** transposes with fluorides, forming *hydrofluoric acid*, **HF** (739 *a*). The gas is distinguished from other substances by *etching hard glass*—previously prepared by coating imperviously with (melted) wax, and writing through the coat. The

operation may be conducted in a small leaden tray, or cup formed of sheet lead; the pulverized fluoride being mixed with sulphuric acid to the consistence of paste.

**741.** If the fluoride be mixed with **silicic acid**, we have, instead of hydrofluoric acid, *silicon fluoride*,  $\text{SiF}_4$  (739 *b*); a gas which does not attack glass, but when passed into water produces hydrofluosilicic acid,  $\text{H}_2\text{SiF}_6$  (739 *c*, *d*) (742).\*

Also, heated with acid sulphate of potassium, in the dry way, fluorides disengage hydrofluoric acid. If this operation be performed in a small test-tube, the surface of the glass above the material is corroded and roughened:



By heating a mixture of borax, acid sulphate of potassium, and a fluoride, fused to a bead on the loop of platinum wire, in the clear flame of the Bunsen gas-lamp, an evanescent *yellowish-green color* is imparted to the flame.

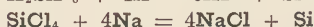
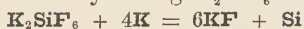
**742. HYDROFLUOSILICIC ACID**,  $(\text{HF})_2\text{SiF}_4$ , or  $\text{H}_2\text{SiF}_6$ , prepared as directed in the note to 741, forms metallic *silicofluorides*, mostly soluble in water; those of barium, sodium, and potassium, being only slightly soluble in water, and made quite insoluble by addition of alcohol. The silicofluorides are precipitated translucent and gelatinous. With concentrated sulphuric acid, they disengage hydrofluoric acid, **HF**. By heat, they are resolved into fluorides and silicon fluoride: as,  $\text{BaF}_2 + \text{SiF}_4$ .

## SILICON. Si = 28.195.

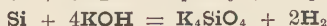
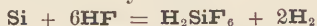
**743. Occurrence.**—It is never found in nature in a free state, but always combined with oxygen in the form of silicon dioxide,  $\text{SiO}_2$ , as quartz, opal, flint, sand, etc. All geological formations except chalk contain silicon, as the dioxide or as a silicate.

**Preparation and Properties.**—There are three modifications of silicon.

(1) **Amorphous silicon**, made by fusing  $\text{K}_2\text{SiF}_6$  with K, or  $\text{SiCl}_4$  with Na.



It is a dark-brown powder, sp. gr. 2.0. Non-volatile and infusible; burns in the air, forming  $\text{SiO}_2$ ; and in chlorine, forming  $\text{SiCl}_4$ . Not attacked by acids, except **HF**; but dissolved by **KOH**.



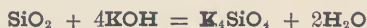
(2) **Graphoidal silicon** is made by fusing the amorphous with **Al**, and then dissolving the **Al** with **HCl**. It fuses in, but is not oxidized by, oxygen; **HF** has no action on it; but is dissolved in a mixture of **HF** and **HNO}\_3**,  $\text{H}_2\text{SiF}_6$  being produced. Fused **KOH** acts slowly upon it. (3)

\* *Hydrofluosilicic acid* is directed to be prepared by taking one part each of fine sand and finely-powdered fluor-spar, with six to eight parts of concentrated sulphuric acid, in a small stoneware bottle or a glass flask, provided with a wide delivery-tube, dipping into a little mercury in a small porcelain capsule, which is set in a large beaker containing six or eight parts of water. The stoneware bottle or flask is set in a small sand-bath, with the sand piled about it, as high as the material, and gently heated from a lamp. Each bubble of gas decomposes with deposition of gelatinous silicic hydrate. When the water is filled with this deposit, it may be separated by straining through cloth and again treating with the gas for greater concentration. The strained liquid is finally filtered and preserved for use.



**Adamantine** silicon is formed by fusing the graphoidal. It looks like hematite, and is oxidized with greater difficulty than the other modifications.

**744. Silicic Anhydride**, or silica,  $\text{Si}^{\text{IV}}\text{O}_2$ , is a stable, non-volatile, infusible solid; insoluble in water or acids, soluble in fixed alkali hydrate solutions, by formation of silicates. These are formed as normal salts, quadribasic; metasalts, dibasic; and in many other proportions of base and acid.



**745.** Of the **Silicates**, only those of potassium and sodium are **soluble** in water. The solutions of alkali silicates somewhat resemble, in the nature of their union, the alkaline solutions of zinc, aluminium, and lead. These silicates in solution are decomposed by all acids, including carbonic, with separation of silicic acid,  $\text{H}_4\text{SiO}_4$ , gelatinous. Silicic acid is soluble, silicic anhydride insoluble, in the mineral acids. Some of the insoluble silicates are also dissolved by sulphuric and by hydrochloric acid, with separation of gelatinous silicic acid. Other silicates are dissolved by these acids, when heated in closed tubes at about  $200^\circ \text{C}$ . Soluble silicates precipitate, from salts of non-alkali metals, silicates insoluble in water, but mostly soluble in acids.

Silicates are **determined**, qualitatively or quantitatively, by the separation of the anhydride, **746**.

**746.** Silicic acid is obtained as  $\text{H}_2\text{SiO}_3$ ,  $\text{H}_4\text{SiO}_4$ , and other hydrates of  $\text{SiO}_2$ . It is decomposed by evaporation to dryness, with a residue of silica, insoluble in acids.—Hence, when an alkali silicate is *acidulated* (with hydrochloric or nitric acid), and *evaporated strictly to dryness* on the water-bath, and again treated with water and the same acid, the silica is left behind insoluble. This behavior is characteristic for silicic acid, and serves for its **separation** as well as detection.

The formation of the alkali silicate, from *silica or an insoluble silicate*, as the first step in this operation, is generally obtained in the dry way, by **fusion** with three or four parts of mixed **carbonates of sodium and potassium** in a porcelain crucible. (These carbonates, mixed in about molecular proportions, fuse at a much lower temperature than either alone.)—Also, the soluble silicates may be formed by boiling with solution of potassium or sodium hydroxide, as stated in **744**; the operation being performed in a silver or platinum vessel. Silica dissolves, with more or less readiness, in boiling solution of potassium or sodium carbonate.

Silica is not soluble in **ammonium hydroxide**, and the salts of ammonium separate gelatinous silica from solutions of potassium or sodium silicate. Therefore, in operating with these solutions, silica is precipitated with the bases of the third group:



**747.** In the fused **bead** of microcosmic salt, particles of silica *swim un-*

*dissolved*. If a silicate be taken, its base will, in most cases, be dissolved out, leaving a “*skeleton of silica*” undissolved in the liquid bead.—But with a bead of sodium carbonate, silica (and most silicates) fuse to a clear *glass* of silicate.

For the reactions of silica with fluorides, see 739.

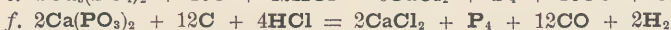
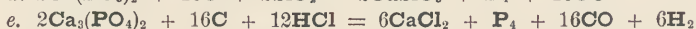
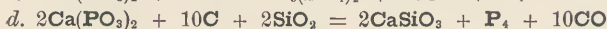
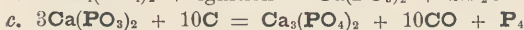
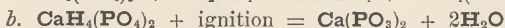
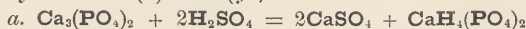
**748.** Silica is separated from the fixed alkalis in natural silicates, by mixing the latter in fine powder with three parts of precipitated calcium carbonate, and one-half part of ammonium chloride, and heating in a platinum crucible to redness for half an hour, avoiding too high a heat. On digesting in hot water, the solution contains all the alkali metals, as chlorides, with calcium chloride and hydrate. [J. LAWRENCE SMITH.]

### PHOSPHORUS. P = 30.958.

**749.** *Specific gravity* of the solid, 1.814; of the liquid, 1.7555 (DAMIEN, 1881); of the red, 2.34 (TROOST, 1875). Vapor density ( $H = 1$ ), 62, indicating that its molecule is  $P_4$ . Yellow phosphorus melts at  $44.4^\circ C.$  ( $112^\circ F.$ ), and boils at  $287.3^\circ C.$  ( $549^\circ F.$ ) (PISATI, 1875). Under pressure of 26.2 atmospheres boils at  $511^\circ C.$  ( $952^\circ F.$ ) (TROOST, 1873). Red phosphorus melts at  $255^\circ C.$  ( $491^\circ F.$ ) (ODLING).

**Occurrence.**—It is never found free in nature. It is found in the primitive rocks as calcium phosphate, occasionally as aluminium, iron, or lead phosphate, etc. Plants extract it from the soil, and animals from the plants. Hence traces of it are found in nearly all animal and vegetable tissues; more abundantly in the seeds of plants and in the bones of animals.

**Preparation.**—(1) From bones. They are first burned, which leaves a residue, consisting chiefly of  $Ca_3(PO_4)_2$ ; then  $H_2SO_4$  is added, producing soluble calcium tetrahydrogen diphosphate (*a*). After filtering from the insoluble calcium sulphate it is ignited, leaving calcium metaphosphate (*b*). Then fused with charcoal, reducing two-thirds of the phosphorus to the free state (*c*). The admixture of sand,  $SiO_2$ , with the charcoal is preferred, in which case the whole of the phosphorus is reduced (*d*). Hydrochloric acid passed over red hot calcium phosphate and charcoal reduces the whole of the phosphorus. This process works well in the laboratory, and has also been successfully employed on a larger scale. Either of the calcium phosphates may be used (*e*) and (*f*).



**750. Properties of Yellow or Ordinary Phosphorus.**—It has a transparent, slightly yellowish color, but turns white at the surface after some

time. Its odor, sometimes described as garlic, which it scarcely resembles, is well known. It is very poisonous; one-half a grain has proved fatal. When inhaled in small quantities, as in match-making, it causes toothache, followed by decay of the teeth; later aching of the jaw, followed by decay of the jaw. A trace of it dissolves in water. Alcohol dissolves 0.4, ether 0.9, olive oil 1.0, and turpentine 2.5 per cent. of it, while carbon disulphide dissolves 10 to 15 times its own weight. It oxidizes in the air at high temperatures to  $\text{H}_3\text{PO}_4$ ; at lower temperatures, or with an insufficient supply of air, to  $\text{H}_3\text{PO}_3$ .

Phosphorus is luminous in the dark. This luminosity is the result of slow combustion. It is not luminous at  $0^\circ \text{C}$ . Its luminosity increases with the temperature, and if exposed freely to the air the heat of combustion raises its temperature, until at  $44^\circ \text{C}$ . it bursts into flame. It is best preserved under water. In a fine state of division, such as is produced by its evaporation from the carbon disulphide solution, it takes fire at once at temperatures in which the compact phosphorus can be kept for days.

Boiled with alkali or alkaline earth hydroxides, it forms a hypophosphite and phosphorus hydride,  $\text{PH}_3$ . Phosphorus is largely used in match-making. Yellow phosphorus is used in the ordinary match, and the red (amorphous) in the safety matches, the phosphorus being on a separate surface. Phosphorus is usually estimated as a phosphate after oxidation with  $\text{HNO}_3$ .

**751. Oxidation.**—In presence of water, **Cl**, **Br**, and **I** form **HCl**, **HBr**, **HI**, and  $\text{H}_3\text{PO}_4$ . Chloric, bromic, and iodic acids give the same products. When dry, finely-divided phosphorus is mixed with substances which readily part with oxygen, such as potassic chlorate or metallic peroxides; very slight friction is sufficient to cause the explosive oxidation of the phosphorus. When sodic carbonate is heated to redness with phosphorus, the carbonic anhydride is reduced and carbon is set free. Owing to its affinity for oxygen, phosphorus acts as a powerful reducing agent. Platinum, gold, silver, and copper are deposited in a metallic state when white phosphorus is left in contact with the solution of their salts.

**752. Red or Amorphous Phosphorus.**—When ordinary phosphorus is heated for 40 hours at  $240^\circ \text{C}$ . to  $250^\circ \text{C}$ ., the red variety is formed; but if the heat is allowed to rise above  $260^\circ \text{C}$ . it is again changed to ordinary phosphorus; but under pressure ordinary phosphorus heated to  $300^\circ \text{C}$ . is immediately and completely changed to the red. If finely divided it has a scarlet-red color; in larger particles it has a dull or brownish-red color. It is odorless, tasteless, non-poisonous, and non-luminous in the dark.

It is insoluble in water, ether, or carbon disulphide. It requires no special precaution for its preservation; does not (if free from traces of the other variety) oxidize in the air, and does not ignite until heated to  $240^\circ \text{C}$ . ( $464^\circ \text{F}$ .) **HNO**<sub>3</sub>, **Cl**, **Br**, and **I** act as upon the ordinary phosphorus,

but more slowly. A black variety of phosphorus is formed by suddenly cooling the melted ordinary phosphorus to  $0^{\circ}$  C. This and the white opaque crust which forms on ordinary phosphorus have not been much studied.

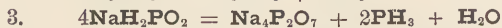
### PHOSPHORUS HYDRIDE. $\text{PH}_3$ .

Oxidation valence..... $\text{P}^{'''}\text{H}'_3$

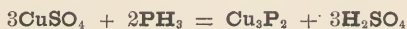
Structural valence..... $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{P}-\text{H} \end{array}$

Vapor density, 17, indicating that the molecule is  $\text{PH}_3$ .

**753. Preparation.**—(1) By boiling phosphorus in an alkali or an alkaline earth. (2) By ignition of  $\text{H}_3\text{PO}_2$  or  $\text{H}_3\text{PO}_3$ . (3) By ignition of hypophosphite of the alkalis or alkaline earths. (4) By action of calcium or magnesium phosphide on water or  $\text{HCl}$ .



**Properties.**—A colorless gas having a very disagreeable odor. It is liquefied by pressure and cold. As usually prepared, it is spontaneously inflammable. It is a strong reducing agent; transposes many metallic solutions—*e.g.*,  $\text{CuSO}_4$ . It reduces solutions of gold and silver to the metallic state. It burns in the air, forming water and metaphosphoric acid. It is oxidized by hot  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ , chlorine-water, hypochlorites,  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{HNO}_3$ ,  $\text{H}_3\text{AsO}_4$ , etc.



A liquid phosphorus hydride,  $\text{P}_2\text{H}_4$ , and a solid,  $\text{P}_4\text{H}_2$ , are known.

### HYPOPHOSPHOROUS ACID. $\text{H}_3\text{PO}_2$ .

Oxidation valence..... $\text{H}'_3\text{P}'\text{O}^{''}_2$

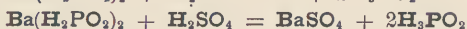
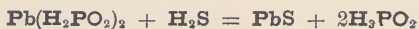
Structural valence..... $\begin{array}{c} \text{H}^* \\ | \\ \text{H}-\text{O}-\text{P}=\text{O} \\ | \\ \text{H} \end{array}$

**754.** The anhydride,  $\text{P}_2\text{O}$ , has not been obtained. The acid is formed :  
(1) By transposing lead hypophosphite with  $\text{H}_2\text{S}$ ; or the barium salt with

\* The structural formula represents the atom of phosphorus as holding three positive bonds (toward oxygen) and two negative bonds (toward hydrogen), so that the sum of its valence is one ( $\text{P}^{'''}-\text{O}^{''}=\text{O}$ ). See paragraph 614.

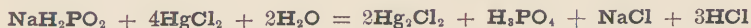


$\text{H}_2\text{SO}_4$  added in exactly molecular proportions; or by treating the calcium salt with a like quantity of  $\text{H}_2\text{C}_2\text{O}_4$ .



**Properties.**—By evaporation in a vacuum the liquid  $\text{H}_3\text{PO}_2$  is obtained, which, on cooling to  $174^\circ \text{C}$ ., solidifies (THOMPSON, 1874). In forming salts only one-third of the hydrogen of the acid is displaced—*e.g.*, sodium hypophosphite is  $\text{NaH}_2\text{PO}_2$ , not  $\text{Na}_3\text{PO}_2$ . It rapidly oxidizes if exposed to the air, forming phosphoric acid. Heat decomposes it, forming  $\text{PH}_3$  and  $\text{H}_3\text{PO}_4$  (or  $\text{HPO}_3$  if at a red heat). On ignition hypophosphites leave pyrophosphites, evolving  $\text{PH}_3$ . Hypophosphorous acid may be known from phosphorous acid by adding cupric sulphate to the free acid and heating the solution to  $55^\circ \text{C}$ . ( $131^\circ \text{F}$ .) With hypophosphorous acid a reddish-black precipitate of copper hydride ( $\text{Cu}_2\text{H}_2$ ) is thrown down, which, when heated in the liquid to  $100^\circ \text{C}$ . ( $212^\circ \text{F}$ .), is decomposed with the deposition of the metal and the evolution of hydrogen, whilst with phosphorous acid the metal is precipitated and hydrogen evolved, but no  $\text{Cu}_2\text{H}_2$  is formed. Further, hypophosphorous acid reduces the permanganates immediately, but phosphorous acid only after some time. Phosphites precipitate barium, strontium, and calcium salts, while hypophosphites do not. When hypophosphorous acid is treated with zinc and sulphuric acid it is converted into phosphoretted hydrogen. On boiling hypophosphorous acid with excess of alkali hydroxide, first a phosphite then a phosphate is formed, with evolution of hydrogen.

**Estimation.**—(1) By oxidation with nitric acid and then proceeding as with phosphoric acid. (2) By mercuric chloride acidulated with  $\text{HCl}$ ; the temperature must not rise above  $60^\circ \text{C}$ ., otherwise metallic mercury will be formed. The precipitated  $\text{Hg}_2\text{Cl}_2$ , after washing and drying at  $100^\circ \text{C}$ ., is weighed.



**755. Production of Hypophosphites.**—All ordinary metals form hypophosphites except tin, copper, and mercurousm. Silver and ferric hypophosphites are very instable. (1) A few metals, such as zinc and iron, dissolve in  $\text{H}_3\text{PO}_2$ , giving off hydrogen and forming a hypophosphite. (2) The alkali and alkaline earth salts may be formed by boiling phosphorus with the hydroxides. (3) As all hypophosphites are soluble, none can be formed by precipitation. All may be formed from their sulphates by transposition with barium hypophosphite. (4) All may be made by adding  $\text{H}_3\text{PO}_2$  to the carbonates or hydroxides of the metals.

**756. Oxidation.**—In all cases an excess of the oxidizing agent produces phosphoric acid or a phosphate. Perhaps the best method of proving that  $\text{H}_3\text{PO}_2$  is all changed to  $\text{H}_3\text{PO}_4$  is that it fails to blacken argentic nitrate.

The reduction of mercuric chloride is sometimes preferred, especially if hydrochloric acid is present.

Where the oxidation is not fully complete, first remove any phosphate which may be present as an impurity, by addition of magnesium sulphate in presence of ammonium chloride and ammonium hydroxide; then, after oxidation, repeat the process to prove partial oxidation.

**HNO<sub>2</sub>** and **HNO<sub>3</sub>** *a.* Become **NO**.

**H<sub>2</sub>SO<sub>3</sub>** *b.* Becomes free sulphur.

**H<sub>2</sub>SO<sub>4</sub>** *c.* Becomes first sulphurous acid, then sulphur.

**Cl** *d.* Becomes hydrochloric acid, and phosphoric acid is formed; with alkalis a chloride is formed.

**HClO** *e.* Becomes hydrochloric acid. With alkalis a chloride is formed.

**HClO<sub>3</sub>** *f.* Becomes hydrochloric acid. Prove same as above.

**Br** *g.* Forms hydrobromic acid.

The action takes place also in alkaline mixture, forming a bromide.

**HBrO<sub>3</sub>** *h.* Forms hydrobromic acid.

**I** *i.* Forms hydriodic acid; and in alkaline mixture an iodide.

**HIO<sub>3</sub>** *j.* Forms hydriodic acid.

**H<sub>6</sub>Fe<sub>2</sub>(CN)<sub>12</sub>** *k.* Forms ferrocyanic acid. In this case the formation of the same cannot be proven by addition of ferric chloride, because an excess of hypophosphorous acid changes ferric chloride to ferrous chloride, which then gives a precipitate with ferrieyanide of potassium. A good method is to add a slight excess of fixed alkali, and then an excess of alcohol which will precipitate the ferrocyanide of potassium, which may, after washing with alcohol, be dissolved in water and tested in the usual way.

**Pb<sup>'''</sup>** *l.* Becomes **Pb''** both in presence of fixed alkali and acids.

**Ag'** *m.* Becomes **Ag°** " " " "

**Hg'** *n.* Becomes **Hg°** " " " "

**Hg''** *o* Becomes **Hg°** " " " "

**As<sup>v</sup>** and **As<sup>'''</sup>** *p.* Become metallic arsenic (in presence of hydrochloric acid).

**Bi<sup>'''</sup>** *q.* Becomes **Bi''**. The action takes place both in presence of alkalis and acetic acid.

**Cu''** *r.* Becomes **(Cu<sub>2</sub>)''** or **Cu<sub>2</sub>H<sub>2</sub>**, and, on boiling, metallic copper is formed. See 754.

**Mn''<sup>+n</sup>** *s.* In presence of acids gives **Mn''**. (No action in presence of alkalis.)

**Mn<sup>vii</sup>** *t.* With alkalis gives **Mn<sup>iv</sup>**.

With acids gives **Mn''**.

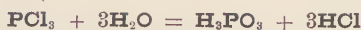
$\text{Co}'''$	<i>u.</i>	Becomes $\text{Co}''$ .	No action in alkaline mixture.
$\text{Ni}'''$	<i>v.</i>	Becomes $\text{Ni}''$ .	“ “
$(\text{Fe}_2)^{\text{VI}}$	<i>w.</i>	Becomes $\text{Fe}''$ .	“ “
$\text{Cr}^{\text{VI}}$	<i>x.</i>	Becomes $\text{Cr}'''$ .	“ “

PHOSPHOROUS ACID.  $\text{H}_3\text{PO}_3$ .Oxidation valence..... $\text{H}_3\text{P}^{\text{III}}\text{O}^{-''}_3$ 

$\begin{array}{c} \text{H} \\ | \\ \text{O} \\ | \\ \text{H}-\text{O}-\text{P}-\text{O}-\text{H} \end{array}$ 
 or
  $\begin{array}{c} \text{O} \\ || \\ \text{H}-\text{O}-\text{P}-\text{O}-\text{H} \\ | \\ \text{H} \end{array}$

Structural valence . . . . .

757. Phosphorus anhydride,  $\text{P}_2\text{O}_3$ , is formed by the combustion of phosphorus at a low temperature or in a limited supply of air. It is a volatile, crystalline solid, inflammable, and having a garlic-like odor. It cannot be formed by heating  $\text{H}_3\text{PO}_3$ , which would produce  $\text{H}_3\text{PO}_4$  and  $\text{PH}_3$ . Heated in a sealed tube it decomposes thus:  $5\text{P}_2\text{O}_3 = 3\text{P}_2\text{O}_5 + \text{P}_4$ . Phosphorous acid is formed by the action of water upon the anhydride or upon the trichloride.



Two atoms of its hydrogen, rarely only one, are displaced by metals—*e.g.*,  $\text{K}_2\text{HPO}_3$ ,  $\text{PbHPO}_3$ ,  $\text{BaHPO}_4$ . It is a strong reducing agent, oxidizing to phosphoric acid when exposed to the air. Reduces salts of silver and gold to the metallic state. It is changed to phosphoric acid by most of the strong oxidizing acids, and by many of the higher metallic oxides.

PHOSPHORIC ACID  $\text{H}_3\text{PO}_4$ Oxidation valence..... $\text{H}_3\text{P}^{\text{V}}\text{O}^{-''}_4$ 

$\begin{array}{c} \text{O} \\ || \\ \text{H}-\text{O}-\text{P}-\text{O}-\text{H} \\ | \\ \text{O} \\ | \\ \text{H} \end{array}$

Structural valence.....

758. Phosphoric anhydride,  $\text{P}_2\text{O}_5$ , is prepared by burning phosphorus in oxygen or air. It cannot be formed by heating  $\text{H}_3\text{PO}_4$ , which would form volatile metaphosphoric acid,  $\text{HPO}_3$ . It is a white, flaky, deliquescent solid, fusible, subliming unchanged at a red heat. It dissolves in water, forming three varieties of phosphoric acid: (1) Metaphosphoric acid,  $\text{HPO}_3$ . (2) Pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ . (3) Orthophosphoric acid,  $\text{H}_3\text{PO}_4$ .

759. Metaphosphoric acid,  $\text{HPO}_3$ ,\* is made by the action of cold water

\* For structural formula see *Remsen's Theoretical Chemistry*, 3d ed., p. 185.

on  $P_2O_5$ , or by the action of a red heat upon  $H_3PO_4$  or  $H_4P_2O_7$ . Also by action of  $H_2S$  on the lead salt, or of  $H_2SO_4$  on the barium salt. It is slowly changed to  $H_3PO_4$  by boiling with water.

**Metaphosphates** are especially distinguished, by the means mentioned in 769 and 771. Also, they are not precipitated by solutions of magnesium salts with ammonium hydroxide, unless very concentrated, or by the molybdate solution. The *silver precipitate*,  $AgPO_3$ , *white*, is soluble in alkali metaphosphate solutions, distinction from pyrophosphates.

**Free** metaphosphoric acid precipitates solutions of silver nitrate, lead nitrate, and lead acetate, the precipitates being insoluble in excess of metaphosphoric acid, and soluble in moderately dilute nitric acid. Barium, calcium, and ferrous chlorides, and magnesium, aluminium, and ferrous sulphates, are not precipitated by free metaphosphoric acid. Ferric chloride is precipitated, a distinction from orthophosphoric acid. See 769.

There are various polymeric modifications of metaphosphoric acid, distinguished from each other chiefly by physical differences of the acids and their salts. Pure metaphosphoric acid is a white, viscid, or waxy solid. (Ordinary glacial phosphoric acid owes its hardness to the universal presence of sodium metaphosphate.)

Fusion with excess of sodium carbonate converts both metaphosphates and pyrophosphates to normal orthophosphate.

**760.** Pyrophosphoric acid,  $H_4P_2O_7$ ,\* is formed by heating  $H_3PO_4$  to  $215^\circ C.$ , or by the action of  $H_2S$  on the lead salt and by the action of  $H_2SO_4$  on the barium salt.

**Pyrophosphates** are precipitated from their solutions by **silver nitrate**, as *silver pyrophosphate*,  $Ag_4P_2O_7$ , *white*, soluble in ammonium hydrate and in nitric acid.

The *pyrophosphates of the alkaline earth metals* are difficultly soluble in **acetic acid**. The most of the pyrophosphates of the heavy metals, except silver, are soluble in solutions of alkali pyrophosphates, as *double pyrophosphates soluble* in water (distinctions from orthophosphates).

Ammonium molybdate reacts but slowly with pyrophosphate solutions—and not until orthophosphate is *formed by digestion with the nitric acid* of the reagent solution.

**Magnesium salts with ammonium hydroxide** give a precipitate of double *pyrophosphate*, soluble in alkali pyrophosphate solution.

**Free** pyrophosphoric acid gives precipitates with solutions of silver nitrate, lead nitrate or acetate, and ferric chloride; no precipitates with barium or calcium chloride, or with magnesium or ferrous sulphate. (Further, see 769.)

**761.** Orthophosphoric acid is made: (1) By boiling  $P_2O_5$ ,  $HPO_3$ , or  $H_4P_2O_7$  in water. (2) By boiling phosphorus in dilute nitric acid. (3) By the combustion of  $PH_3$  in moist air. (4) By action of water on  $PCl_5$ .

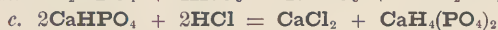
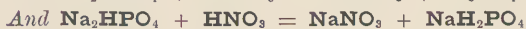
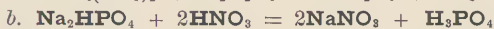
\* For structural formula see *Remsen's Theoretical Chemistry*, 3d ed., p. 185.



**Orthophosphoric acid**,  $\text{H}_3\text{PO}_4$ , is a translucent, feebly crystallizable, and very deliquescent soft solid; reduced by heat first to pyrophosphoric acid, then to metaphosphoric acid, which is volatile.

Orthophosphoric acid is formed from phosphorus by oxidation in water; and from metaphosphoric acid or pyrophosphoric acid by digesting with dilute mineral acids, or even by long boiling in water, or, as sodium salt, by fusion with excess of sodium carbonate.

Phosphoric acid is formed from metallic phosphates by transposition with acids in cases where a precipitate results, as a lead or barium phosphate with sulphuric acid, or silver phosphate with hydrochloric acid. But when the products are all soluble, as calcium phosphate with acetic acid or sodium phosphate with sulphuric acid, the transposition is only partial; so that unmixed phosphoric acid is not obtained. A non-volatile acid, like phosphoric, is not separated from liquid mixtures, as the volatile acids are, like hydrochloric. The change represented by equation (a) can be so verified that pure phosphoric acid will be separated, but the changes shown in equations (b) and (c) do not comprise the whole of the material taken. In the operation (b) some sodium phosphate and some nitric acid will be left, and in (c) some trihydrogen phosphate will no doubt be made.



**762.** The **Orthophosphates**, *dimetallic and trimetallic*, are **insoluble in water**—except those of the metals of the ordinary alkalis. They are all, however, more or less soluble in aqueous phosphoric acid by formation of *monometallic* salts, as  $\text{CaH}_4(\text{PO}_4)_2$ , having an acid reaction. Lithium phosphate is nearly insoluble in water. Phosphates are insoluble in alcohol.

In **analysis**, the molybdate precipitate (768) is most distinctive. Separation by the ferric phosphate precipitate in presence of acetic acid (306) is employed. Separation from oxalate, as calcium precipitate, by acetic acid, is used in systematic qualitative work (764). Ignition test: see 771.

**763.** **Soluble salts of all metals, except those of the alkalis**, precipitate solutions of ordinary phosphates (dimetallic and trimetallic orthophosphates).

**764.** Soluble salts of the alkaline earth metals, with **dimetallic** alkali phosphates, as  $\text{Na}_2\text{HPO}_4$ , form white precipitates of *phosphates, two-thirds metallic*, as  $\text{CaHPO}_4$ ; with **trimetallic** alkali phosphates, white precipitates of *phosphates, normal* or full metallic, as  $\text{Ca}_3(\text{PO}_4)_2$ . The precipitates are soluble in acetic acid, and in the stronger acids (761 c). Concerning the ammonium magnesium phosphate, see 79.

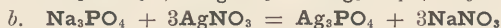
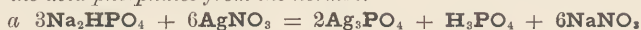
**765.** Solutions of orthophosphates give, with soluble ferric, chromic, and aluminium salts, mostly the normal *phosphates*,  $\text{Fe}_2(\text{PO}_4)_2$ , etc. The *ferric phosphate* is but slightly soluble in acetic acid, and for this reason it is made the *means of separating phosphoric acid from metals* of the earths and alkaline earths (306). Solution of sodium or potassium acetate is

added ; and if the reaction is not markedly acid, it is made so by addition of Acetic Acid. Ferric chloride (if not present) is now added, drop by drop, avoiding an excess. The precipitate, *ferric phosphate*, is brownish-white.

With zinc and manganous salts, the precipitate is dimetallic or normal— $\text{ZnHPO}_4$ , or  $\text{Zn}_3(\text{PO}_4)_2$ —according to the conditions of precipitation. Manganic salts give a colored solution, as explained in 252. With salts of nickel, a light green normal phosphate is formed ; with cobalt, a reddish normal phosphate.

**766.** Silver salts precipitate normal *silver phosphate*,  $\text{Ag}_3\text{PO}_4$ , light yellow, soluble in acetic and nitric acids and in ammonium hydroxide. The color of the silver precipitate distinguishes ortho- from pyro-phosphoric acid. Lead salts precipitate mostly  $\text{Pb}_3(\text{PO}_4)_2$ , but slightly soluble in acetic acid. Bismuth salts form  $\text{BiPO}_4$ , peculiar in being insoluble in dilute nitric acid. Copper forms a bluish-white precipitate, either normal or two-thirds metallic. Mercurous salts precipitate *mercurous phosphate*,  $\text{Hg}_6(\text{PO}_4)_2$ , white. Mercuric nitrate (not the chloride) precipitates mercuric phosphate,  $\text{Hg}_3(\text{PO}_4)_2$ , white.

**767.** If a disodium or dipotassium orthophosphate is added to solution of silver nitrate, free acid is formed, and an acid reaction to test-paper is induced (*a*). But with a trisodium or tripotassium phosphate, the solution remains neutral (*b*)—a means of distinguishing the acid phosphates from the normal.



**768. Ammonium Molybdate**, in its nitric acid solution (604), furnishes an exceedingly delicate test for phosphoric acid, giving the pale yellow precipitate, termed *ammonium phosphomolybdate*. The molybdate should be in excess, therefore it is better to add a little of the solution tested (which must be neutral or acid) to the reagent, taking a half to one cub. cent. of the latter in a test-tube. For the full delicacy of the test, it should be set aside, at 30° to 40° C., for several hours.

**769. Free orthophosphoric acid** is not precipitated by ordinary salts of third and fourth group metals (in instance of ferric chloride, a distinction from pyrophosphoric acid and metaphosphoric acid),\* but is precipitated in part by silver nitrate, and lead nitrate and acetate. **Ammoniacal solution of calcium chloride** or of barium chloride precipitates free orthophosphoric acid.

\* A solution containing 5 p. c. *ferric chloride*, mixed with one-fourth its volume of a 10 p. c. solution of *orthophosphoric acid*, requires that near half of the latter be neutralized (so that phosphate is to phosphoric acid as 1.114 is to 1.000) before precipitation occurs. On the other hand, 4 c. c. of a 5 p. c. solution of ferric chloride, mixed with 1 c. c. of a 6 p. c. solution of *metaphosphoric acid*, form a precipitate, to dissolve which 30 c. c. of the same metaphosphoric acid solution or 5 c. c. of a 24 p. c. solution of hydrochloric acid are required. Four c. c. of a 5 p. c. solution of *silver nitrate* with 1 c. c. of a 10 p. c. solution of *orthophosphoric acid* give a precipitate, to dissolve which requires 7 c. c. of the same orthophosphoric acid solution. [The Author's report of work by Mr. Morgau, *Am. Jour. Phar.*, xlviii. (1876), 534.]

**770.** Orthophosphoric acid—or an orthophosphate with acetic acid—*does not coagulate egg albumen or gelatine*. This is a distinction of both orthophosphoric acid and pyrophosphoric acid *from metaphosphoric acid*.

**771. Ignition with metallic magnesium** (or sodium) reduces phosphorus from phosphates to magnesium *phosphide*,  $P_2Mg_3$ , recognized by odor of  $PH_3$ , formed on contact of the phosphide with water. A bit of magnesium wire (or of sodium) is covered with the previously ignited and powdered substance in a glass tube of the thickness of a straw, and heated. If any combination of phosphoric acid is present, vivid incandescence will occur, and a black mass will be left. The latter, crushed and wet with water, gives the odor of phosphorus hydride.

#### SULPHUR. S = 31.984.

**772.** *Specific gravity*, 1.95 to 2.05. *Melting point*,  $114.5^\circ C.$  ( $238^\circ F.$ ) (BRODIE). *Vapor density* ( $H=1$ ) above  $800^\circ C.$  is 32, showing that the molecule is  $S_2$ ; but at  $480^\circ C.$  it is 96, showing that the molecule at that temperature is  $S_6$ .

**Occurrence.**—(1) Found in a free state, and as  $SO_2$  in volcanic districts. (2) As  $H_2S$  in some mineral springs. (3) As a sulphide. Iron pyrites,  $FeS_2$ ; copper pyrites,  $CuFeS_2$ ; orpiment,  $As_2S_3$ ; realgar,  $As_2S_2$ ; blende,  $ZnS$ ; cinnabar,  $HgS$ ; galena,  $PbS$ . (4) As a sulphate. Gypsum,  $CaSO_4 + 2H_2O$ ; heavy spar,  $BaSO_4$ ; kieserite,  $MgSO_4 + H_2O$ ; bitter spar (epsom salts),  $MgSO_4 + 7H_2O$ ; glauber salt,  $Na_2SO_4 + 10H_2O$ , etc.

**Preparation.**—(1) The native sulphur is separated from the clay and rock in which it is embedded, partly by melting and partly by distillation. (2) From  $FeS_2$  by heating in close cylinders  $3FeS_2 = Fe_3S_4 + S_2$ ; or at a higher temperature  $FeS_2 = FeS + S$ . Much of the sulphur contained in pyrites is converted into and utilized as sulphuric acid.

**773. Properties.**—Sulphur is a solid—in yellow, brittle, friable *masses* (from melting); or in yellowish, gritty *powder* (from sublimation); or in nearly white, slightly cohering, finely crystalline *powder* (by precipitation from its compounds). It melts at about  $114.5^\circ C.$  ( $238^\circ F.$ ); at higher temperatures, it suffers peculiar physical modifications of consistence, etc.; and distils at  $448.4^\circ C.$  It is not sensibly volatile at ordinary temperatures, but has a slight, characteristic odor.

In chemical activity, volatility, and other properties, sulphur stands as the second member of the Oxygen Series: O, 15.9633; S, 31.984; Se, 78.797; Te, 127.96.

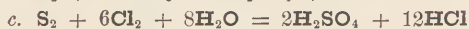
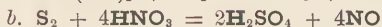
Sulphur is insoluble in water; slightly soluble in alcohol and in ether, freely soluble in carbon disulphide; but with physical solvents other than water, its different modifications have different solubilities.

On being heated it melts at  $114.5^\circ C.$  to a pale yellow liquid; as the temperature rises it grows darker and thicker, until at about  $180^\circ C.$  it is nearly solid, so that the dish may be inverted without spilling. At  $260^\circ C.$

it again becomes a liquid as at first; and at  $448.4^{\circ}$  C. it boils and is converted into a brownish-red vapor. If it is slowly cooled, exactly the same physical changes take place in the reverse order, becoming thick at  $180^{\circ}$  C. and thin again at  $114.5^{\circ}$  C., and at lower temperatures solid. If, at a temperature near its boiling point, it is poured into cold water, it forms a soft, ductile, elastic string, resembling india-rubber. In a few hours this ductile sulphur changes back to the ordinary form, the change evolving heat. But if poured into water from the other liquid form—that is, at  $114.5^{\circ}$  C.—it forms only ordinary, brittle sulphur. *Ordinary and precipitated* sulphur is soluble in  $\text{CS}_2$ ; the ductile variety is insoluble. Frequently commercial samples are found to contain a definite per cent. of one of the insoluble varieties.

**774. Oxidation.**—Sulphur, when fused with the following elements, combines with them to form sulphides: **Pb, Ag, Hg, Sn, As, Sb, Bi, Cu, Cd, Zn, Co, Ni, Fe, Sr, Ca, Mg, K, Na, In, Tl, Pt, Pd, Rh, Ir, Li, Ce, La, Di.**

Sulphur *dissolves* readily in hot solutions of hydroxides of potassium, sodium, calcium, or barium, forming *supersulphides and thiosulphates* (a). These can be separated by alcohol, in which the sulphides dissolve. Sulphur is acted upon slowly by active oxidizing agents, as hot concentrated nitric acid (b), or chlorine generated in presence of water (c), with formation of *sulphuric acid*. Hot concentrated sulphuric acid very slowly oxidizes sulphur to *sulphurous anhydride*, by its own reduction to the same compound (d):



In the air, at ordinary temperatures, finely divided sulphur is very slightly oxidized, by ozone, to *sulphuric acid*; at about  $260^{\circ}$  C. ( $500^{\circ}$  F.) it begins to oxidize rapidly to *sulphurous anhydride*, burning with a blue flame.

$\text{S}^{\text{VI}-n}$  becomes  $\text{S}^{\text{VI}}$  when fused with alkaline carbonate and nitrate or chlorate. That is, free sulphur,  $\text{S}^0$ , or any compound containing sulphur with less than six bonds, is oxidized to a sulphate if fused with an alkaline nitrate or chlorate, nitric oxide or a chloride being formed and carbon dioxide escaping.

### HYDROSULPHURIC ACID. $\text{H}_2\text{S}$ .

Oxidation valence..... $\text{H}'_2\text{S}^{-n}$

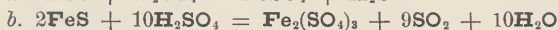
Structural valence..... $\text{H}-\text{S}-\text{H}$

**775.** *Vapor density* ( $\text{H} = 1$ ), 17. *Melting point* (freezing point),  $-85.5^{\circ}$  C. ( $-122^{\circ}$  F.) (FARADAY). *Boiling point*,  $-61.8^{\circ}$  C. ( $-79.3^{\circ}$  F.) (REGNAULT). Becomes a liquid at  $10^{\circ}$  C. ( $50^{\circ}$  F.) under a pressure of 17 atmospheres.



**Occurrence.**—Found in volcanic gases and in many mineral springs. Its presence in spring-water is accounted for by the reduction of sulphates to sulphides by organic matter and subsequent liberation of  $\text{H}_2\text{S}$  by carbonic acid.

**776. Preparation.**—For laboratory use it is prepared by action of dilute acids (usually  $\text{H}_2\text{SO}_4$ ) upon ferrous sulphide. The ferrous sulphide is prepared either by fusion of the iron with the sulphur, or by bringing red hot iron rods in contact with sticks of sulphur. The ferrous sulphide melts as fast as formed, and is made to drop into a tub of cold water. Dilute  $\text{H}_2\text{SO}_4$  should be used (*a*). Concentrated  $\text{H}_2\text{SO}_4$  has no action on  $\text{FeS}$ , unless heated, and then  $\text{SO}_2$  is evolved (*b*); and frequently free sulphur is formed (if only a little water is present) by the action of the  $\text{H}_2\text{S}$  upon the  $\text{H}_2\text{SO}_4$  first formed. Hydrosulphuric acid is slowly formed if hydrogen be passed through melted sulphur; also if sulphur be fused with tallow or paraffine, and when organic substances (*e.g.*, eggs) containing sulphur are allowed to decay.



**777. Properties.**—It is a colorless, poisonous gas, having the odor of rotten eggs. By pressure and cold it may be condensed, first to a liquid, then to a solid. At  $0^\circ \text{C}$ . water dissolves 4.37, and at  $15^\circ \text{C}$ . 2.66, volumes of the gas.

The solution in open vessels **vaporizes** gas constantly, at ordinary temperatures, until exhausted; more rapidly when boiled. Both gas and solution feebly redden moist **litmus paper**; and have a very strong, characteristic odor. (The concentrated gas is a quick poison, by inhalation.)

Absolute hydrosulphuric acid is combustible in the air—burning with a blue flame to sulphurous anhydride and water.

**778.** The **solubility** of the **Metallic Sulphides** in water, dilute acids, hot nitric acid, and in alkali sulphides, is shown in the grouping of the bases, and the sub-grouping of the second-group precipitates.

In **analysis**, sulphides are known by generation of  $\text{H}_2\text{S}$  (779), or separation of **S** by oxidizing solvents, and by the color test with nitroferri cyanide (782).

**779. Sulphuric acid**, dilute, transposes the metallic sulphides; except those of arsenic, tin, mercury, silver (and lead), which are decomposed with difficulty, or not at all:



The gaseous hydrosulphuric acid, when liberated, is recognized by its odor, by blackening paper moistened with **lead acetate**, or with a solution of a **lead salt with excess of potassium** or sodium hydroxide (388 and 387). In the detection of traces of the gas, a slip of bibulous paper, so moistened, may be inserted into a slit in the smaller end of a cork, which

is fitted to the test-tube, wherein the material to be tested is treated with sulphuric acid ; the tube being set aside in a warm place for several hours. A very delicate test is made by conducting the gas into ammoniacal solution of nitroferri cyanide (782).

If any oxidizing agents are present—as chromates, ferric salts, manganic salts, chlorates, etc.—hydrosulphuric acid is not generated, but instead sulphur is separated, or sulphates are formed (780).

The sulphides not transposed with hydrochloric or sulphuric acid, are recognized by the *separation of sulphur* on treatment with **nitric acid**, or with **nitrohydrochloric acid**. Also, these sulphides and certain super-sulphides, attacked with difficulty by acids, as *iron pyrites* and *copper pyrites*, are reduced and dissolved, with evolution of *hydrosulphuric acid*, by **dilute sulphuric acid with zinc**. The gas, with its excess of hydrogen, may be tested by 782.

**780.** Hydrosulphuric acid is a strong **reducing agent**, and the metallic sulphides act in the same capacity with a greater or less degree of force. The reactions with oxidizing agents are given at length in 785.

The hydrogen of  $H_2S$  takes oxygen readily ; the sulphur more slowly. In the oxidation of metallic *sulphides*, generally, less sulphur is left unoxidized than occurs in the oxidation of hydrosulphuric acid—owing to the stronger tendency to form *sulphates*.

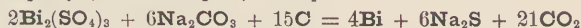
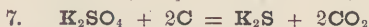
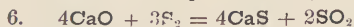
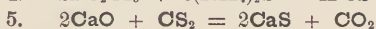
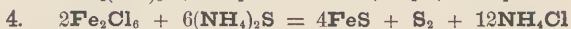
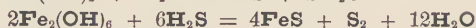
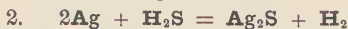
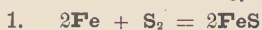
**781.** Solutions of metallic sulphides give precipitates with soluble **salts of second and third group metals** ; hydrogen sulphide, with salts of second-group metals only. The precipitates are *sulphides*, except with chromium and aluminium ; reduction occurring with ferric and arsenic salts, which form ferrous and arsenious sulphides. The precipitates have strongly marked **colors**—that of zinc being *white* ; those of iron, copper, and lead, *black* ; arsenic, *yellow* ; antimony, *orange-red* ; mercury, successively white, yellow, orange, and *black*.

**782.** Solutions of **nitroferri cyanides** (693) give, with soluble metallic sulphides (or with hydrosulphuric acid after addition of an alkali, or with free sulphur after digesting with an alkali), an intense, rich *purple color*, disappearing after some time. Add a drop of the reagent, to a few drops of the solution, on a white porcelain surface. Vapors are tested for hydrosulphuric acid by conducting them into ammoniacal solution of sodium nitroferri cyanide. (Vapors are tested for ammonia by passing them into solution of nitroferri cyanide with hydrosulphuric acid.)

**783.** By ignition in the air, sulphur gives its characteristic odor of *sulphurous anhydride*. Many of the *sulphides* yield more or less sulphurous anhydride ; most of them are also, partly or wholly, converted to sulphates.

When ignited on **charcoal with sodium carbonate**—or (*distinction from sulphates*) *if ignited in a porcelain crucible* with sodium carbonate—soluble *sodium sulphides* are obtained. The production of the sodium sulphide is proved by the *black stain* of  $Ag_2S$ , formed on metallic **silver** by a moistened portion of the fused mass. (Compounds of selenium and tellurium, 612.)

**784. Formation of Sulphides.**—(1) By fusion of the metals with sulphur, see 774. (2) By action of  $\text{H}_2\text{S}$  upon the free metals, hydrogen being evolved. With **Hg** and **Ag** this occurs at ordinary temperature, but with most metals a higher temperature is needed. (3) Action of  $\text{H}_2\text{S}$  on metallic oxides or hydroxides. Those sulphides which are decomposed by water (*e.g.*,  $\text{Al}_2\text{S}_3$ ,  $\text{Cr}_2\text{S}_3$ ) are not formed in its presence, but by action of  $\text{H}_2\text{S}$  upon the oxide at a red heat. (4) By action of soluble sulphides upon metallic solutions. The ordinary sulphides of the first three groups are formed thus, except ferric salts, which are precipitated as **FeS**, and aluminium and chromic salts as hydroxides. (5) By action of  $\text{CS}_2$  upon oxides at a red heat. (6) By action of free sulphur upon oxides at a red heat. (7) By the action of charcoal upon the oxyacids of sulphur at a red heat in presence of an alkaline carbonate.



**Estimation.**—The sulphur in sulphides is oxidized by nitric acid, or chlorine, or by fusion with sodium carbonate and nitrate, and, after precipitation with barium chloride, weighed as barium sulphate.

**785. Oxidation.**—*a.* Free sulphur liberated from hydrosulphuric acid may sometimes be recognized simply by its appearance. But when white precipitates are formed at the same time, the whole should be allowed to settle, then the sulphur dissolved in carbon disulphide, and again separated by evaporation, or precipitated from the carbon disulphide solution by addition of alcohol, and then further tested by 773.

For action upon **HNO<sub>2</sub>** and **HNO<sub>3</sub>**, see 713 and 733.

**H<sub>2</sub>SO<sub>3</sub>** *b.* Forms water and sulphur [*Watts' Dictionary*, 3, 203].

Sometimes, especially if the moist gases are used, pentathionic acid,  $\text{H}_2\text{S}_5\text{O}_6$ , is formed.  $10\text{SO}_2 + 10\text{H}_2\text{S} = 2\text{H}_2\text{S}_5\text{O}_6 + 8\text{H}_2\text{O} + 5\text{S}_2$ .

**H<sub>2</sub>SO<sub>4</sub>** *c.* No action if the sulphuric acid is dilute.

With strong acid, sulphur and sulphurous anhydride are formed.

To prove the latter, add sulphuric acid to dry ferrous sulphide and boil, or pass hydrosulphuric acid gas into hot sulphuric acid, and **SO<sub>2</sub>** will be evolved.

**Cl** *d.* Forms first sulphur, and finally sulphuric and hydrochloric acids.

This takes place in alkaline mixture also, forming a sulphate.

**HClO** *e.* Same as above.

- HClO<sub>3</sub>** *f.* With excess of hydrosulphuric acid, free sulphur and hydrochloric acid are formed. With excess of **HClO<sub>3</sub>**, sulphuric acid is formed.
- Br** *g.* Forms hydrobromic acid and sulphur. In alkaline mixture a sulphate is formed.
- HBrO<sub>3</sub>** *h.* Forms sulphur and hydrobromic acid; with excess of **HBrO<sub>3</sub>**, sulphuric acid is formed.
- I** *i.* Forms sulphur and hydriodic acid.
- HIO<sub>3</sub>** *j.* With excess of hydrosulphuric acid, hydriodic acid and sulphur are formed.
- H<sub>2</sub>Fe<sub>2</sub>(CN)<sub>12</sub>** *k.* Forms potassium ferrocyanide and sulphur.  
*Proof:* Boil to expel excess of hydrosulphuric acid, then add ferric chloride.
- PbO<sub>2</sub>** *l.* Forms **PbS** and sulphur.
- As<sup>v</sup>**. **As<sub>2</sub>S<sub>3</sub>** and free sulphur are formed.
- Mn''** + *n* *m.* Forms **Mn''** and (**S<sub>2</sub>**)°. That is, all compounds of manganese having more than two bonds are reduced to the dyad, and free sulphur is formed.
- K<sub>2</sub>Mn<sub>2</sub>O<sub>8</sub>** *n.* With potassium sulphide, potassium sulphate is formed [*M. Schlagdenhafien, Bulletin de la Société Chimique* (2), 22, 16; and *Jour. Chem. Society*, 28, 912].  $4\text{K}_2\text{Mn}_2\text{O}_8 + 3\text{K}_2\text{S} = 3\text{K}_2\text{SO}_4 + 4\text{K}_2\text{O} + 8\text{MnO}_2$ . This method he uses quantitatively for the estimation of hydrosulphuric acid. With some dilute free acid, such as sulphuric, hydrosulphuric added in excess to potassium permanganate gives manganous sulphate and free sulphur.
- H<sub>2</sub>CrO<sub>4</sub>** *o.* Forms chromic oxide and sulphur.
- Ni<sub>2</sub>O<sub>3</sub>** *p.* Becomes nickelous sulphide and sulphur.
- Co<sub>2</sub>O<sub>3</sub>** *q.* Forms cobaltous sulphide and sulphur.
- (Fe<sub>2</sub>)<sup>vi</sup>** *r.* Forms **Fe''** and sulphur. The action takes place in either alkaline or acid mixture.

### THIOSULPHURIC ACID. **H<sub>2</sub>S<sub>2</sub>O<sub>3</sub>**.

Oxidation valence.....**H<sub>2</sub>S'<sub>2</sub>O''**,

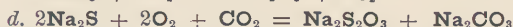
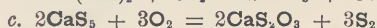
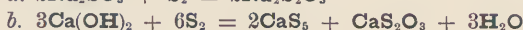
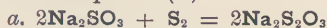
Structural valence..... $\text{H}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\text{S}-\text{H}$ , or  $\text{H}-\text{O}-\overset{\overset{\text{S}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\text{O}-\text{H}$  \*

**786.** Thiosulphuric acid (formerly called hyposulphurous acid) has not been isolated. Thiosulphates are made by boiling sulphur in a soluble sul-

\* In union with oxygen the chemical polarity of sulphur is positive; in union with hydrogen, sulphur is negative; in union of sulphur with sulphur, the polarities of the one side are neutralized by those of the other side, so that in this union the total polarity of the sulphur stands at 0. See paragraph 614.  
 $\text{S}^{\text{vi}} + \text{S}^{-''} = (\text{S}_2)^{\text{iv}}$ .  
 A. B. P.



phite (*a*), or in a soluble hydroxide (*b*); also by exposure of the persulphides of the alkalies and alkaline earths to the air (*c*). The carbon dioxide and oxygen of the air act upon the normal sulphides of the fixed alkalies to produce a thiosulphate (*d*).



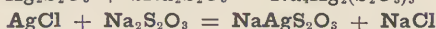
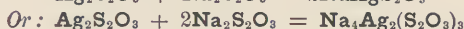
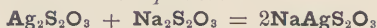
When thiosulphates are decomposed by acids, the constituents of thiosulphuric acid are dissociated as sulphurous acid and sulphur. Nearly all acids in this way decompose thiosulphates:



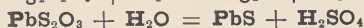
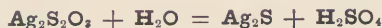
The larger number of the thiosulphates are **soluble in water**; those of barium, lead, and silver being only very sparingly soluble. The thiosulphates are insoluble in alcohol. They are decomposed, but not fully dissolved, by acids, the decomposition leaving a residue of sulphur.

In **analysis**, thiosulphates are distinguished by giving a precipitate of sulphur with evolution of sulphurous anhydride when their solutions are treated with hydrochloric acid (789); by their intense reducing power (790), shown in the blackening of the silver precipitate (788); and by non precipitation of calcium salts.

**787.** Alkali thiosulphate solutions dissolve the thiosulphates of lead, silver, and mercury; also, the chloride, bromide, and iodide of silver, and mercurous chloride; the iodide and sulphate of lead; the sulphate of calcium, and some other precipitates—by formation of soluble *doubtful thiosulphates*:



**788.** Barium chloride forms, in solutions of thiosulphates, a white precipitate of *barium thiosulphate*,  $\text{BaS}_2\text{O}_3$ , nearly insoluble in water; dissolving in acids, except the sulphur residuc.—Calcium chloride forms no precipitate (distinction from sulphite).—Solutions of **silver nitrate** (420), **lead acetate**, and **mercurous nitrate** form at first *white precipitates of thiosulphates*, soluble in excess of alkali thiosulphates, as stated in the preceding paragraph. These white precipitates, by standing, or quickly by warming, turn darker and finally *black*, by formation of *sulphides*, with sulphuric acid.



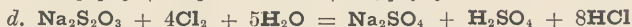
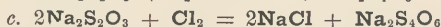
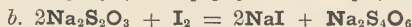
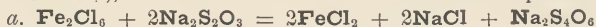
Solution of copper salts, with thiosulphates, on long standing, precipitate cuprous salt, changed by boiling to cuprous sulphide and sulphuric acid, as above. For the precipitation of sulphides of **arsenic**, **antimony**, and, in the cold, **tin**, see 562.

**789.** The *precipitation of sulphur with evolution of sulphurous anhydride*, by addition of **dilute acids**—as **hydrochloric** or **acetic**—is characteristic of thiosulphates. It will be understood, however, that in pres-

ence of oxidizing agents, which can be brought into action by the acid, sulphides will likewise give a precipitate of sulphur (780).

**790.** Thiosulphates are **Reducing Agents**—even stronger and more active than the sulphites, to which they are so easily converted. This reducing power is exemplified by the conversion of **ferric salts** into ferrous salts (*a*), and by the bleaching of **iodine** solutions (*b*), both of which changes are so sharply defined that they are useful in volumetric analysis.

If the ferric solution be made red by addition of a few drops of thiocyanate, the exact point of complete reduction is made obvious : while the inevitable color of free iodine is nearly sufficient to mark the point when loss of color shows that all the iodine has entered into combination, but the addition of starch-paste renders the indication more exact. In both these reactions, the oxidation of the thiosulphate changes it into a *tetra-thionate*, as  $\text{Na}_2\text{S}_4\text{O}_6$  (*c*), but with excess of chlorine the hexad sulphur is produced (*d*).



In other changes, sulphuric acid is frequently formed. By greater or less degrees of oxidation, thiosulphates reduce chromic acid to chromic salts; permanganic acid, first to manganates (green), then to manganic salts; bromic and iodic acids first to bromine and iodine, and then, respectively, to hydrobromic and hydriodic acids; nitric acid to nitrogen oxides; and arsenic acid to arsenious compounds.

**791.** On **ignition**, or by heat short of ignition, all thiosulphates are decomposed. Those of the alkali metals leave sulphates and polysulphides (*a*), others yield sulphurous acid with sulphides, or sulphates, or both. The capacity of thiosulphates for rapid oxidation, renders their mixture with chlorates, nitrates, etc., *explosive*, in the dry way. **Chlorates** with hyposulphites explode violently in the mortar. **Cyanides** and ferricyanides, fused with thiosulphates, form thiocyanates, which may be dissolved by alcohol from other products. By fusion on charcoal with  $\text{Na}_2\text{CO}_3$ , thiosulphates form sulphides (*b*) and (*c*); and by fusion with an alkaline carbonate and nitrate or chlorate, a sulphate is formed (*d*).

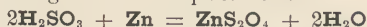


### DITHIONOUS ACID. $\text{H}_2\text{S}_2\text{O}_4$

Oxidation valence..... $\text{H}_2\text{S}'''\text{O}''_4$

Structural valence..... $\text{H}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\text{S}}-\overset{\overset{\text{O}}{\parallel}}{\text{S}}-\text{O}-\text{H}$

**792.** Prepared by treating zinc with sulphurous acid.

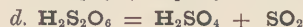
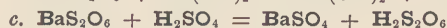
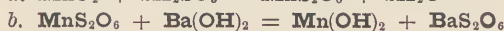
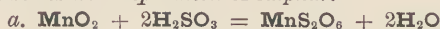


The yellow solution thus formed is a powerful reducing agent; bleaches prussian blue, and reduces salts of silver, mercury, and copper to the metallic state; absorbs oxygen rapidly from the air, becoming sulphurous acid, or a sulphite. It is employed for estimating dissolved oxygen in water. Formerly (SCHUTZENBERGER, 1869) this acid was supposed to be  $\text{H}_2\text{SO}_2$ , and was called by some hydrosulphurous acid; by others hyposulphurous acid.

DITHIONIC ACID.  $\text{H}_2\text{S}_2\text{O}_6$ .Oxidation valence..... $\text{H}'_2\text{S}^{\text{v}}_2\text{O}^{-''}_6$ 

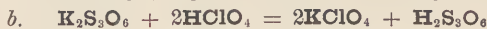
Structural valence..... $\text{H}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\text{O}-\text{H}$

793. The manganous salt is first prepared by action of  $\text{SO}_2$  at  $0^\circ \text{C}$ . upon  $\text{MnO}_2$  (a); after treating with  $\text{Ba}(\text{OH})_2$  (b); the resulting barium salt is transposed by  $\text{H}_2\text{SO}_4$  (c). It is a colorless solution, bears concentration in a vacuum until it has a specific gravity of 1.347; farther attempts to concentrate, or heat alone decomposes it (d). Exposure to the air converts it into  $\text{H}_2\text{SO}_4$  (e). All dithionates are soluble, and are decomposed by heat in presence of  $\text{HCl}$  without separation of sulphur. Boiling decomposes all other acids of the thionic series *with separation of sulphur*.

TRITHIONIC ACID.  $\text{H}_2\text{S}_3\text{O}_6$ .Oxidation valence..... $\text{H}'_2(\text{S}_3)^{\text{x}}\text{O}^{-''}_6$ 

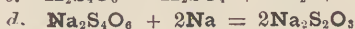
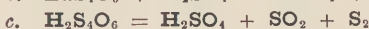
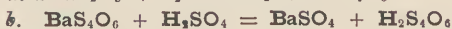
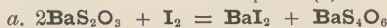
Structural valence..... $\text{H}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\text{O}-\text{H}$

794. The potassium salt is prepared by boiling  $\text{KHSO}_3$  with sulphur (a); and addition of  $\text{HClO}_4$  precipitates  $\text{KClO}_4$  (b). The acid has been obtained in crystals; it is instable, decomposing by heat or on standing, as shown in (c).

TETRATHIONIC ACID.  $\text{H}_2\text{S}_4\text{O}_6$ .Oxidation valence..... $\text{H}'_2(\text{S}_4)^{\text{x}}\text{O}^{-''}_6$ 

Structural valence..... $\text{H}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\text{O}-\text{H}$

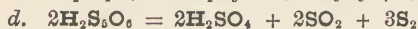
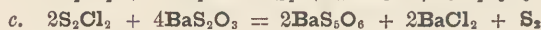
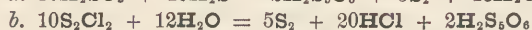
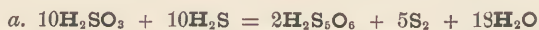
795. The barium salt is formed by adding iodine to the thiosulphate (a); from which the acid is transposed by  $\text{H}_2\text{SO}_4$  (b). The acid decomposes on boiling as is shown in (c). Sodium amalgam reconverts it into the thiosulphate (d).



PENTATHIONIC ACID.  $\text{H}_2\text{S}_5\text{O}_6$ .Oxidation valence..... $\text{H}'_2\text{S}''_5\text{O}^{-''}_6$ 

Structural valence..... $\text{H}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\text{S}-\text{S}-\text{S}-\overset{\overset{\text{O}}{\parallel}}{\underset{\underset{\text{O}}{\parallel}}{\text{S}}}-\text{O}-\text{H}$

**796.** Formed by passing hydrogen sulphide into a solution of sulphurous acid (*a*); also by action of water upon  $\text{S}_2\text{Cl}_2$  (*b*). The barium salt is formed by action of  $\text{S}_2\text{Cl}_2$  upon barium thiosulphate (*c*). It may be concentrated in a vacuum until it has a specific gravity of 1.6; farther concentration or boiling heat alone decomposes it, as is shown in (*d*).





797. *Reactions to distinguish Tetra- and Pentathionic Acids from each other, and from the other Thionic Acids.*<sup>a</sup>

Reagents.	Dithionic acid, $\text{H}_2\text{S}_2\text{O}_6$ .	Trithionic acid, $\text{H}_2\text{S}_3\text{O}_6$ .	Tetrathionic acid, $\text{H}_2\text{S}_4\text{O}_6$ .	Pentathionic acid, $\text{H}_2\text{S}_5\text{O}_6$ .
Potassium hydroxide.....	No precipitate.....	No precipitate.....	No precipitate.....	Immediate precipitate of sulphur, redissolving gradually on standing, if not in much excess and coagulated.
Dilute hydrochloric acid....	No action.....	Evolution of $\text{SO}_2$ , and precipitate of S.	No action.....	No action.
Mercurous nitrate .....	No precipitate.....	Immediate black precipitate, becoming white on standing.	Yellow precipitate, gradually darkening.	At first yellow precipitate, turning white with excess of reagent on standing.
Silver nitrate.....	No precipitate.....	Yellow precipitate, soon becoming black.	Yellow precipitate, soon turning black, and also on adding ammonium hydroxide.	Yellow precipitate, gradually darkening; black on adding ammonium hydroxide.
Ammoniacal silver nitrate....	.....	No brown coloration, even on standing. On warming, $\text{Ag}_2\text{S}$ formed.	No dark or brown coloration, even on standing, <i>unless warmed</i> .	Almost immediate brown coloration, becoming black on warming.
Mercuric cyanide.....	No precipitate.....	.....	At first yellow precipitate; turns black on warming, with evolution of $\text{HCN}$ .	At first yellow precipitate, gradually turning black on heating, with evolution of $\text{HCN}$ .
Mercuric chloride .....	No precipitate.....	Yellow precipitate, becoming white with excess of reagent.	On warming, white precipitate.....	On warming, whitish yellow precipitate.
Potassium sulph-hydrate solution ( $\text{KHS}$ ).	.....	.....	White precipitate of sulphur.....	White precipitate of sulphur.
Dilute solution of potassium permanganate.	One drop, immediate brown precipitate.	One drop, immediate brown precipitate, even in presence of dilute $\text{H}_2\text{SO}_4$ .	Decolorized, without addition of dilute $\text{H}_2\text{SO}_4$ .	Decolorized, without addition of dilute $\text{H}_2\text{SO}_4$ .

<sup>a</sup> TAKAMATSU and SMITH, *Jour. Chem. Soc.*, **37**, 608.

SULPHUROUS ACID.  $\text{H}_2\text{SO}_3$ .

Oxidation valence of the anhydride and acid...  $\text{S}^{\text{IV}}\text{O}^{--}_2$ ,  $\text{H}'_2\text{S}^{\text{IV}}\text{O}^{--}_3$

Structural valence of the anhydride and acid...  $\text{O}=\text{S}=\text{O}$ ,  $\text{H}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{O}-\text{H}$

**798.** Vapor density of the anhydride ( $\text{H} = 1$ ), 32. *Melting point*,  $-76^\circ \text{C}$ . (FARADAY). *Boiling point*,  $-10^\circ \text{C}$ . (PICTET, 1877). At a pressure of not more than four atmospheres is liquefied at  $35^\circ \text{C}$ . (PICTET).

**Occurrence**—Found free in volcanic gases.

**Preparation.**—(1) By burning sulphur in the air. (2) By heating sulphur with metallic oxides. (3) By decomposition of thiosulphates and of all the thionic acids. (4) By dissociation of  $\text{H}_2\text{SO}_4$  by heat, see 734. (5) For laboratory use it is generally made by action of hot concentrated  $\text{H}_2\text{SO}_4$  upon copper or other metals. (6) By action of hot concentrated  $\text{H}_2\text{SO}_4$  upon sulphur, or (7) upon charcoal. (8) By heating anhydrous sulphates with sulphur.

1.  $\text{S}_2 + 2\text{O}_2 = 2\text{SO}_2$
2.  $\text{MnO}_2 + \text{S}_2 = \text{MnS} + \text{SO}_2$   
 $4\text{ZnO} + 3\text{S}_2 = 4\text{ZnS} + 2\text{SO}_2$   
 $4\text{Fe}_2\text{O}_3 + 7\text{S}_2 = 8\text{FeS} + 6\text{SO}_2$   
 $2\text{Pb}_2\text{O}_4 + 5\text{S}_2 = 6\text{PbS} + 4\text{SO}_2$
3.  $2\text{Na}_2\text{S}_2\text{O}_3 + 4\text{HCl} = 4\text{NaCl} + 2\text{SO}_2 + \text{S}_2 + 2\text{H}_2\text{O}$
5.  $\text{Cu} + 2\text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$
6.  $\text{S}_2 + 4\text{H}_2\text{SO}_4 = 6\text{SO}_2 + 4\text{H}_2\text{O}$
7.  $\text{C} + 2\text{H}_2\text{SO}_4 = 2\text{SO}_2 + \text{CO}_2 + 2\text{H}_2\text{O}$
8.  $\text{FeSO}_4 + \text{S}_2 = \text{FeS} + 2\text{SO}_2$

**799. Properties.**—Sulphurous anhydride,  $\text{SO}_2$ , is a colorless liquefiable gas, of a powerful, characteristic, suffocating odor and effect, that of burning sulphur. It bleaches litmus-paper. It is not combustible in the air. It dissolves readily in water, doubtless as sulphurous acid; the solution saturated at  $15^\circ \text{C}$ . ( $60^\circ \text{F}$ .) containing about 14 per cent. of the sulphur dioxide; an increase of temperature greatly decreasing its solubility.

**800.** It may be supposed that the solution, at ordinary temperatures, is a mixture of water and  $\text{H}_2\text{SO}_3$ —a view resting on somewhat stronger support than we have for considering the solution of carbonic anhydride to contain  $\text{H}_2\text{CO}_3$ .

**801. Solution of Sulphurous Acid** first reddens litmus, and then bleaches it. It decomposes carbonates with effervescence. It has a strong odor from vaporization of sulphurous anhydride, which is soon completely expelled on boiling. By exposure to air it is gradually oxidized to sulphuric acid, from which it is seldom entirely free (812).

**802. The Sulphites** of the metals of the alkalies are freely soluble in water; the normal sulphites of all other metals are insoluble, or but very slightly soluble in water. The sulphites of the metals of the alkaline earths,

and some others, are soluble in solution of sulphurous acid—the solution being precipitated on boiling. The alkali bases form acid sulphites (“bi-sulphites”), which can be obtained in the solid state, but evolve sulphurous anhydride. The sulphites are insoluble in alcohol.

In **analysis**, sulphites are recognized by the odor of the anhydride, liberated by adding an acid (799). Also, by the reducing power (808) and by oxidation to sulphate (807).

**803.** Solution of sulphurous acid (free from sulphuric acid) is but slightly precipitated by solutions of salts—owing to the solubility of sulphites in acids.

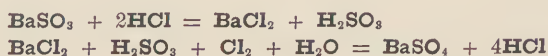
*Sulphites are decomposed by all acids ; except carbonic and boracic, and, in some instances, hydrosulphuric.*

**804.** *Solutions of metallic sulphites are precipitated by the soluble salts of all metals except those of the alkalies. The precipitates, mostly white, are soluble in acetic acid ; also, by hydrochloric acid, except first-group sulphites, which are changed to chlorides, and, so far as not oxidized to sulphates, in dilute nitric acid. But these precipitated sulphites are almost invariably accompanied by sulphates which are left undissolved by acids.*

**805.** Solution of **lead acetate** precipitates, from solutions of sulphites, *lead sulphite*,  $\text{PbSO}_3$ , white, easily soluble in dilute nitric acid ; and not blackening when boiled (distinction from thiosulphate). Solution of **silver nitrate** gives a white precipitate of *silver sulphite*,  $\text{Ag}_2\text{SO}_3$ , easily soluble in very dilute nitric acid or in excess of alkaline sulphite, and turning dark-brown when boiled, by formation of metallic silver and sulphuric acid. Solution of **mercuric chloride** produces no change in the cold ; but on boiling, the white *mercurous chloride* is precipitated, with formation of sulphuric acid. Still further digestion, with sufficient sulphite, reduces the white mercurous chloride to gray metallic mercury (equation 448 *b*).

**806.** Solution of **ferric chloride** gives a *red solution of ferric sulphite*,  $\text{Fe}_2(\text{SO}_3)_3$  ; or, in more concentrated solutions, a *yellowish precipitate* of basic ferric sulphite, also formed by addition of alcohol to the red solution. The red solution is decolorized on boiling ; the acid radical reducing the basic radical, and forming ferrous sulphate.

**807.** Solution of **barium chloride** gives a white precipitate of *barium sulphite*,  $\text{BaSO}_3$ , easily soluble in dilute hydrochloric acid—*distinction from sulphate*, which is undissolved, and should be filtered out. Now, on adding to the filtrate **nitrohydrochloric acid**, a precipitate of barium sulphate is obtained—evidence that sulphite has been dissolved by the hydrochloric acid :

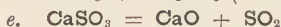
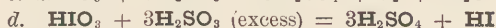
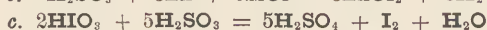
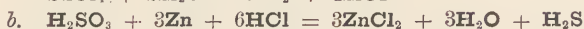
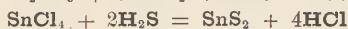


**808.** Sulphurous acid and sulphites are active **Reducing Agents**, by

virtue of their *capacity for oxidation to sulphuric acid and sulphates*. See Oxidations, 813. Reduction by sulphurous acid is exemplified in the precipitations, given above, with silver and mercury, and with barium. Equations for other reductions are given, for chromic acid, 194 *c*; for iodine decoloration, 795 *a*; and for  $\text{HIO}_3$ , 810 (*c*) and (*d*).

809. The reaction with iodic acid is employed as a test for sulphurous acid (as well as for iodic). A mixture of **iodic acid and starch** is turned violet to blue by traces of sulphurous acid or sulphites in vapor or in solution, the color being destroyed by excess of the sulphurous acid or the sulphite.

810. Notwithstanding this ready capacity for oxidation, sulphurous acid is capable of furnishing oxygen, though its power in the latter office is narrowly limited. As an **Oxidizing Agent**, sulphurous acid changes **stannous chloride** to stannic sulphide (*a*); reacts with the nascent hydrogen furnished by **zinc and dilute hydrochloric acid** to form water and *hydrosulphuric acid* (*b*). By **heat alone**, sulphites either split into oxides and sulphurous anhydride (*e*), or into sulphates and sulphides (*f*).



811. **Estimation.**—(1) After converting into  $\text{H}_2\text{SO}_4$  by  $\text{HNO}_3$  or  $\text{Cl}$  it is precipitated by  $\text{BaCl}_2$ , and weighed as  $\text{BaSO}_4$ . (2) The oxidation is effected by fusing with  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  (equal parts). (3) A standard solution of iodine is added, and the excess of iodine determined by a standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$ .

812. **Preparation of sulphites.**—The sulphites of the ordinary metals are usually made by action of sulphurous acid upon the oxides or hydroxides of the metals. They are normal, except mercurous, which is acid, and chromium, aluminium, and copper, which are basic. Sulphurous acid precipitates solutions of metals of the first and second groups, except copper and cadmium.

The sulphites of the alkalis precipitate solutions of the other metals except chromium salts; and some normal sulphites may be made in this manner. The sulphites of silver, mercury, copper, and ferrieum (known only in solution) are instable, the sulphurous acid becoming sulphuric at the expense of the base, which is reduced to a form having a less number of bonds. With the instable stannous sulphite the action is the reverse. (See 810.) All sulphites by exposure to the air slowly absorb oxygen, and are partially converted into sulphates.

813. **Oxidation.**—*a*. Upon other acids sulphurous acid acts as a re-



ducing agent, except with hypophosphorous and hydrosulphuric acids, 756–785. With free metals it acts only as an oxidizing agent. With metallic oxides it is a reducing agent, except with stannous oxide. The method of proof is, in all cases, very simple.

For action on  $\text{HNO}_2$ , see 713; on  $\text{HNO}_3$ , 733; on  $\text{H}_3\text{PO}_2$ , 756; on  $\text{H}_2\text{S}$ , 785.

**Cl** *b.* Forms sulphuric and hydrochloric acids. With alkalies, a sulphate and chloride.

**HClO** *c.* Forms sulphuric and hydrochloric acids.

**HClO<sub>3</sub>** *d.* “ “ “ “ “

**Br** *e.* Forms sulphuric and hydrobromic acids. With alkalies, a sulphate and bromide.

**HBrO<sub>3</sub>** *f.* Forms first bromine, then sulphuric and hydrobromic acids.

**I** *g.* Forms hydriodic and sulphuric acids.

**HIO<sub>3</sub>** *h.* Forms first iodine, then hydriodic and sulphuric acids.

**H<sub>6</sub>Fe<sub>2</sub>(CN)<sub>12</sub>** *i.* Forms ferrocyanic and sulphuric acids.

**PbO<sub>2</sub>** *j.* Forms plumbic sulphate.

**Ag'** *k.* Forms metallic silver. See 805.

**Hg'** and **Hg''** *l.* With the nitrates of mercury, metallic mercury is formed. With mercuric chloride, mercurous chloride is very slowly precipitated, and by long boiling with excess of  $\text{H}_2\text{SO}_3$  metallic mercury is formed.

**Sn''** *m.* With stannous chloride, forms stannic sulphide, or stannic chloride and hydrosulphuric acid, according to the amount of hydrochloric acid present.

**As<sup>v</sup>** *n.* Forms arsenious and sulphuric acids.

**MnO<sub>2</sub>** *p.* If the solution is hot, manganic sulphate is formed [*Watts' Dictionary*, 5, 636]. If cold, manganous dithionate,  $\text{MnS}_2\text{O}_6$ , is formed [*Gmelin's Hand-book*, II. 174].

**Mn''** + *n* becomes **Mn''**. That is, all compounds of manganese having more than two bonds are reduced to the dyad.

**Co<sub>2</sub>O<sub>3</sub>** *q.* Forms **Co''**.

**Ni<sub>2</sub>O<sub>3</sub>** *r.* Forms **Ni''**.

**Fe'''** *s.* Forms **Fe''**.

**Cr<sup>vi</sup>** *t.* Forms chromic sulphate.

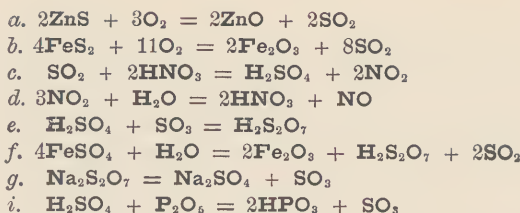
SULPHURIC ACID.  $\text{H}_2\text{SO}_4$ .Oxidation valence.....  $\text{H}'_2\text{S}^{\text{VI}}\text{O}^{\text{--}''}_4$ Structural valence.....  $\text{H}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\text{S}}-\text{O}-\text{H}$ Oxidation valence of pyrosulphuric acid.....  $\text{H}'_2\text{S}^{\text{VI}}_2\text{O}_7$ Structural valence of pyrosulphuric acid.....  $\text{H}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\text{S}}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\text{S}}-\text{O}-\text{H}$ 

**814. Occurrence.**—Found free in the spring water of volcanic districts. Found combined in gypsum,  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ ; in heavy spar,  $\text{BaSO}_4$ ; in celestine,  $\text{SrSO}_4$ ; in epsom salts,  $\text{MgSO}_4 + 7\text{H}_2\text{O}$ ; in glauber salt,  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ , etc.

**815. Preparation.**—Industrially, sulphuric acid is chiefly made by utilizing the  $\text{SO}_2$  evolved as a by-product in roasting various sulphides—*e.g.*, iron and copper pyrites, blende, etc. (a) and (b). The  $\text{SO}_2$  is passed into a large leaden chamber and brought into contact with  $\text{HNO}_3$ , steam, and air. The  $\text{HNO}_3$  first oxidizes a portion of the  $\text{SO}_2$  (c); the steam then reacts upon the  $\text{NO}_2$ , forming  $\text{HNO}_3$  and  $\text{NO}$  (d). This  $\text{NO}$  is at once oxidized again by the air to  $\text{NO}_2$ , so that *theoretically* no nitric acid is lost, but all is used over again. Practically, traces of it are constantly escaping with the nitrogen introduced as air, so that a fresh supply of nitric acid is needed to make up for this loss. The absolute  $\text{H}_2\text{SO}_4$  cannot be made by evaporation or distillation; it still contains about two per cent. of water. It may be made by adding to water, or to the  $\text{H}_2\text{SO}_4$  containing the two per cent. of water, a little more  $\text{SO}_3$  or  $\text{H}_2\text{S}_2\text{O}_7$  than would be needed to make  $\text{H}_2\text{SO}_4$ ; then passing perfectly dry air through it until the excess of  $\text{SO}_3$  is removed, leaving absolute  $\text{H}_2\text{SO}_4$ . Also, if the  $\text{H}_2\text{SO}_4$ , with two per cent. of water, be cooled to  $-34.4^\circ \text{C}$ ,  $\text{H}_2\text{SO}_4$  crystallizes out (REGNAULT); but does not melt again until warmed to  $10.5^\circ \text{C}$ . (MARIGNAC).

**Pyrosulphuric, or Nordhausen sulphuric acid**,  $\text{H}_2\text{S}_2\text{O}_7$ , is made: (e) by solution of sulphuric acid in sulphuric anhydride; (f) by drying  $\text{FeSO}_4 + 7\text{H}_2\text{O}$  until it becomes  $4\text{FeSO}_4 + \text{H}_2\text{O}$ , and then distilling; the distillate, consisting of  $\text{H}_2\text{S}_2\text{O}_7$ , with some  $\text{SO}_2$ . Sulphuric anhydride is made (g) by action of heat on sodium pyrosulphate,  $\text{Na}_2\text{S}_2\text{O}_7$ , prepared by heating  $\text{NaHSO}_4$  to dull redness. (h) By distilling pyrosulphuric acid, the anhydride is collected in an ice-cooled receiver. (i) By heating  $\text{H}_2\text{SO}_4$  with  $\text{P}_2\text{O}_5$ .

A substance having the composition  $\text{S}_2\text{O}_8$ , and called **persulphuric anhydride**, is formed by passing electricity for a long time through a mixture of equal volumes of  $\text{SO}_2$  and oxygen. It is little known.



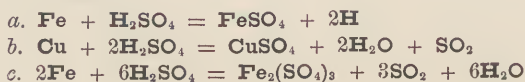
**816.** Sulphuric anhydride,  $\text{SO}_3$ , is a colorless, fibrous, or waxy solid, melting (when recent) at  $25^\circ \text{C}$ . ( $77^\circ \text{F}$ .), boiling at  $46^\circ \text{C}$ . ( $115^\circ \text{F}$ .), and vaporizing with heavy white fumes in the air at ordinary temperatures. It is very deliquescent, and on contact with water combines rapidly, forming sulphuric acid and much heat.

**817.** Absolute sulphuric acid,  $\text{H}_2\text{SO}_4$ , is a colorless, syrupy liquid, having at  $12^\circ \text{C}$ . a specific gravity of 1.842 (MAGRIGNAC, 1870), boiling at  $338^\circ \text{C}$ . ( $640^\circ \text{F}$ .) (MAGRIGNAC). At temperatures above about  $160^\circ \text{C}$ . ( $320^\circ \text{F}$ .) it vaporizes from open vessels, slightly or abundantly, the vapors being white, heavy, and suffocating, exciting coughing without giving premonition by odor. At ordinary temperatures it is strictly non-volatile and inodorous. The sp. gr. of the U. S. P. acid is 1.840.

**818.** It is miscible with water in all proportions with production of heat; it abstracts water from the air (use in desiccators), and quickly abstracts the elements of water from many organic compounds, and leaves their carbon, a characteristic charring effect. It dissolves in alcohol, without decomposing it—but if in sufficient proportion producing ethylsulphuric acid,  $\text{HC}_2\text{H}_5\text{SO}_4$ .

**819.** Sulphuric acid transposes the salts of nearly all other acids, forming sulphates, and either acids (as hydrochloric acid, 839) or the products of their decomposition (as with chloric acid, 860). But salts of mercury, silver, tin, and antimony are with difficulty transposed by sulphuric acid. Also, at temperatures above about  $300^\circ \text{C}$ . (or  $600^\circ \text{F}$ .) phosphoric and silicic acids (and other acids not volatile at this temperature) transpose sulphates, with vaporization of sulphuric acid.

**820.** Sulphuric acid dissolves most metals; though not quite so generally efficient for this purpose as hydrochloric or nitric acid. Diluted sulphuric acid, when cold, dissolves—with evolution of hydrogen—magnesium, aluminium, zinc, iron, manganese, and tin; and, when heated, nickel, cobalt, and cadmium (a). Concentrated sulphuric acid, by application of heat, dissolves—with evolution of sulphurous anhydride—copper, mercury, silver, bismuth, and tin (b) and (c). (Compare 825.) If in a fine state of division all ordinary metals are dissolved, but gold, platinum, iridium, and rhodium are not attacked.



**821.** The metallic Sulphates are freely soluble in water, except those of *barium*, *lead*, *strontium* (very slightly soluble), *calcium*, and *mercurosum*, which are sparingly soluble. For specifications of the solubilities of the sulphates of barium, strontium, and calcium, see 88; of lead, see 389. *Silver* sulphate requires about 200 parts of cold or 100 parts of hot water for solution, and mercurous sulphate is even more sparingly soluble. Bismuth, antimonious and mercuric sulphates are soluble in acidulated water, but decomposed by pure water. The metallic sulphates are insoluble in alcohol (ammonium sulphate sparingly soluble in ordinary alcohol, very slightly in absolute alcohol).

In **analysis**, barium sulphate is chiefly obtained (822). Alcohol is useful for separation of free sulphuric acid from its salts (824).

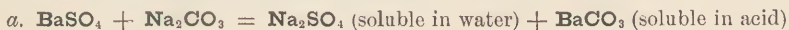
**Acid sulphates** of the alkali bases are formed as crystallizable salts. That of potassium,  $\text{KHSO}_4$ , gives off sulphuric acid above about  $200^\circ \text{C}$ . ( $400^\circ \text{F}$ .), or by greatly diluting its solutions. That of sodium,  $\text{NaHSO}_4$ , is decomposed at a lower temperature, and hardly exists at all in solution. **Alcohol**, added to solutions of the acid sulphates, precipitates the normal sulphates, sulphuric acid remaining in solution :



**822.** Sulphuric acid, or solutions of sulphates, on addition of solutions of **barium salts**, as  $\text{BaCl}_2$ , or  $\text{Ba}(\text{NO}_3)_2$ , give a white precipitate of *barium sulphate*,  $\text{BaSO}_4$ ; insoluble by hydrochloric or nitric acid. This insolubility is a *distinction from all acids*, except selenic and hydrofluosilicic. The precipitate, formed in cold solution, is so fine as to be difficult of removal by filtration; if formed in hot solution and then boiled it is retained by a good filter. The full completion of the precipitate requires that the mixture should stand some time. In strongly acid solutions a precipitate of  $\text{BaCl}_2$ , etc., may be obtained (see 104). A residue of sulphur may appear in this test, applied to thiosulphates (788). Solutions of **lead salts** give a white precipitate of *lead sulphate*,  $\text{PbSO}_4$ ; not transposed with acids, soluble in solution of potassium hydrate. In solutions not dilute, **calcium salts** give a white precipitate of *calcium sulphate*,  $\text{CaSO}_4$ .

**823.** **Alcohol** precipitates the sulphates from their moderately concentrated water solutions; and its addition enables calcium chloride to precipitate the sulphate of calcium in very dilute solutions.

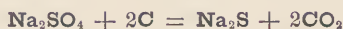
The sulphates insoluble in water are decomposed for analysis—(1st) by long boiling with solution of **alkali carbonate**; and more readily (2d) by fusion with an alkali carbonate. In both cases there are produced—alkali *sulphates* soluble in water, and *carbonates* soluble by hydrochloric or nitric acid, *after* removing the sulphate (*a*). If the fusion be done on charcoal, more or less deoxidation will occur, reducing a part or the whole of the sulphate to sulphide (825), and the carbonate to metal (as with lead, 397), or leaving the metal as a carbonate or oxide (668).





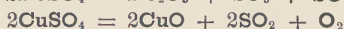
**824.** Free sulphuric acid may be separated from sulphates (except ammonium sulphate) by strong alcohol, solutions being first evaporated nearly to dryness on the water-bath.—A test for free *sulphuric acid, in distinction from sulphates*, may be made (in accordance with 818), by the use of **cane sugar**, as follows: A little of the liquid to be tested is concentrated on the water-bath; then from two to four drops of it are taken on a piece of porcelain, with a small fragment of white sugar, and evaporated to dryness by the water-bath. A greenish-black residue indicates sulphuric acid. (With the same treatment, hydrochloric acid gives a brownish-black, and nitric acid a yellow-brown residue.) A strip of white glazed paper, wet with the liquid tested, by immersing it several times at short intervals, then dried in the oven at 100° C., will be colored black, brown, or reddish, if the liquid contains as much as 0.2 per cent. of sulphuric acid.

**825.** Sulphuric acid and its salts are very stable at ordinary temperatures. They do not at all act as reducing agents—solution of permanganate not being decolorized by sulphuric acid; but at *high temperatures*, they are able to act as **Oxidizing Agents** to some extent. In the action of **metals** on hot concentrated sulphuric acid, there are cases of reduction of the sulphuric to *sulphurous acid*, as stated in 820 *b*; and in the action of **ignited carbon**, we have reduction of sulphates to *sulphides*, in fusion on charcoal, as follows



**826.** It will be observed—sulphates **fused with sodium carbonate on charcoal**, leave a mass which contains sulphides, and, when moistened, stains **metallic silver**; but, when fused with sodium carbonate (on porcelain) *without reducing agents*, leave a mass which, when moistened, *does not stain metallic silver* (distinction from sulphides).

**827.** By **heat alone**, the sulphates of the metals suffer dissociation—some giving off sulphuric anhydride; others, sulphurous anhydride and oxygen:



The sulphates of **Cu, Sb, Fe, Hg, Ni, and Sn** are completely decomposed at a red heat. A white heat decomposes the sulphates of **Al, Cd, Ag, Pb, Mn, and Zn**. An ordinary white heat has no action on the sulphates of the alkalis and alkaline earths; but at the most intense heat procurable the sulphates of **Ba, Ca, and Sr** are changed to oxides; and at the same temperature **K<sub>2</sub>SO<sub>4</sub>** and **Na<sub>2</sub>SO<sub>4</sub>** are completely volatilized, preceded by partial decomposition.

**828.** Sulphates are made, *a*, by dissolving the metals in sulphuric acid, 829; *b*, by dissolving the oxides or hydrates; *c*, by displacement. All salts containing volatile acids are displaced by sulphuric acid and a sulphate formed (except the chlorides of silver, mercury, and tin). The excess of acid may generally be expelled by evaporation, or the crystals washed with cold water or alcohol.

The insoluble sulphates are best made by precipitation.

**829. Oxidation.**—*a*. Sulphuric acid can, of course, never act as a reducing agent, and it does not oxidize the other acids, except hypophosphorous (756), hydrobromic, and hydriodic acids. Some others are decomposed, but not oxidized, and the sulphuric is not reduced. For action on **H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>**, see 652; for **H<sub>3</sub>PO<sub>3</sub>**, 756; for **H<sub>2</sub>S**, 785.

**HBr** *b.* Forms bromine and sulphurous acid. No action occurs except in concentrated solution.

**HI** *c.* Forms iodine and sulphurous acid.

*d.* Metals, when dissolving in dilute sulphuric acid, evolve hydrogen, and form sulphates.

When the metals dissolve in strong sulphuric acid,  $\text{SO}_2$  is evolved, and sulphates are formed.

*Dilute* sulphuric acid does not oxidize any of the metallic oxides.

*Concentrated acid* changes the following :

**Hg<sub>2</sub>O** *e.* Forms mercuric sulphate, and sulphurous anhydride is evolved.

**SnO** *f.* Stannous chloride forms, first, sulphurous anhydride, then hydro-sulphuric acid, stannic chloride at the same time being produced.

**Mn** *g.* With the higher oxides of manganese, dilute sulphuric acid has no action.

**Mn'' + <sup>n</sup>** Forms **Mn''** and ( $\text{O}_2$ )°. That is, all compounds of manganese having more than two bonds are reduced to the dyad ; mangano-sulphate forming and oxygen being evolved.

**Fe''' - <sup>n</sup>** *o.* In hot concentrated  $\text{H}_2\text{SO}_4$  becomes  $\text{Fe}_2(\text{SO}_4)_3$ .

### CHLORINE. $\text{Cl} = 35.370$ .

**830.** Oxidation valence of free chlorine ( $\text{Cl}_2$ )°. See also 613 and 614.

Structural valence of free chlorine, **Cl-Cl**.

*Vapor density* ( $\text{H} = 1$ ), 35.370. The molecule contains two atoms,  $\text{Cl}_2$ . Under ordinary air pressure liquefies at  $-33.6^\circ \text{C}$ . (REGNAULT, 1863) ; and solidifies at  $-102^\circ \text{C}$ . (OLSZEWSKI, 1884). Under pressure of six atmospheres liquefies at  $0^\circ \text{C}$ . (NIEMANN).

**Occurrence.**—It is never found free in nature. It is found in great abundance as sodium chloride.

**831. Preparation.**—(1) *Weldon's process* :  $\text{MnO}_2$  is treated with  $\text{HCl}$ , and the  $\text{MnCl}_2$  formed is precipitated as  $\text{Mn}(\text{OH})_2$  by adding  $\text{Ca}(\text{OH})_2$ . The  $\text{Mn}(\text{OH})_2$  is warmed by steam, and air is blown into it, oxidizing it again to  $\text{MnO}_2$ , and by repeating this process the same manganese is used over again. (2) *Deacon's process* :  $\text{HCl}$ , mixed with air, is passed over fire-bricks moistened with  $\text{CuCl}_2$  and heated to about  $440^\circ \text{C}$ . The heat first changes the  $\text{CuCl}_2$  to  $\text{Cu}_2\text{Cl}_2$ , evolving chlorine ; then the oxygen of the air, aided by the  $\text{HCl}$ , oxidizes the  $\text{Cu}_2\text{Cl}_2$  to  $\text{CuCl}_2$ . It is not certain that the explanation is correct. It is only known that the hydrochloric acid which is passed into the apparatus comes out as free chlorine, and that the copper chloride (small in amount) does not need renewing. (3) By ignition of dry  $\text{MgCl}_2$  in the air. (4) Some chlorides are dissociated by heat alone—*e.g.*,  $\text{PtCl}_4$ ,  $\text{AuCl}_3$ , and  $\text{PdCl}_2$ . (5) By fusing together  $\text{NH}_4\text{NO}_3$ ,

and  $\text{NH}_4\text{Cl}$ . (6) By action of  $\text{HCl}$  upon compounds of  $\text{Mn}'' + n$ ,  $\text{Cr}''' + n$ ,\*  $\text{Co}'' + n$ ,  $\text{Ni}' + n$ ,  $\text{Fe}'' + n$ ,  $\text{Bi}''' + n$ , and  $\text{Pb}'' + n$ , these metallic forms losing  $n$  bonds and becoming chlorides.

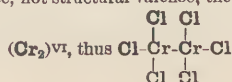
1.  $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$   
 $\text{MnCl}_2 + \text{Ca}(\text{OH})_2 = \text{Mn}(\text{OH})_2 + \text{CaCl}_2$   
 $2\text{Mn}(\text{OH})_2 + \text{O}_2 = 2\text{MnO}_2 + 2\text{H}_2\text{O}$
2.  $2\text{CuCl}_2 + \text{heat} = \text{Cu}_2\text{Cl}_2 + \text{Cl}_2$   
 $2\text{Cu}_2\text{Cl}_2 + \text{O}_2 + 4\text{HCl} = 4\text{CuCl}_2 + 2\text{H}_2\text{O}$
3.  $2\text{MgCl}_2 + \text{O}_2 = 2\text{MgO} + 2\text{Cl}_2$
4.  $\text{PtCl}_4 = \text{Pt} + 2\text{Cl}_2$
5.  $4\text{NH}_4\text{NO}_3 + 2\text{NH}_4\text{Cl} = 12\text{H}_2\text{O} + 5\text{N}_2 + \text{Cl}_2$
6.  $\text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} = 2\text{KCl} + \text{Cr}_2\text{Cl}_6 + 3\text{Cl}_2 + 7\text{H}_2\text{O}$

832. The three elements, chlorine, bromine, and iodine, resemble each other in almost all their properties, reactions, and combinations, differing (as do their atomic weights, 35.37, 79.768, 126.557) with a regular progressive variation; so that their compounds present themselves to us as members of progressive series. In several particulars fluorine (atomic weight, 18.984) corresponds to the first member of this series.

833. **CHLORINE** is a greenish-yellow, suffocating gas, dissolved sparingly by cold water, very slightly by hot water. The solution bleaches litmus; but on standing, the  $\text{Cl}$  is converted into  $\text{HCl}$  (*a*), when it reddens litmus, and is no longer fit for use as a reagent. Chlorine is dissolved freely by alkali hydrates, with combination (*b*), the solution having especial oxidizing force (854). In *distinction from hydrochloric acid*, it bleaches moist litmus, and indigo solution; precipitates sulphur from hydrosulphuric acid, and iodine from solutions of iodides—slight traces of it being revealed by the blue color with solution of **potassium iodide** and **starch**—and acts in presence of water as *a very powerful oxidizing agent* (*a*). It displaces bromine as well as iodine. It dissolves gold-leaf and mercuric sulphide (*distinctions from nitric acid*). Like hydrochloric acid, it precipitates solution of silver nitrate (*c*), and plumbic and mercurous salts; and forms, with vapor of ammonia, a white cloud of  $\text{NH}_4\text{Cl}$ . With ammonium salts, chlorine is liable to cause explosion, nitrogen chloride being formed (+5). For the Oxidations caused by chlorine, see 834.

- a.*  $2\text{Cl}_2 + 2\text{H}_2\text{O} = \text{O}_2 + 4\text{HCl}$
- b.*  $3\text{Cl}_2 + 6\text{KOH} = 5\text{KCl} + \text{KClO}_3 + 3\text{H}_2\text{O}$   
*Or:*  $\text{Cl}_2 + 2\text{KOH} = \text{KCl} + \text{KClO} + \text{H}_2\text{O}$
- c.*  $3\text{Cl}_2 + 6\text{AgNO}_3 + 3\text{H}_2\text{O} = 5\text{AgCl} + \text{AgClO}_3 + 6\text{HNO}_3$

\*  $\text{Cr}'''$  indicates oxidation valence, not structural valence, the latter being



The most important **Acids containing Chlorine** are :

Hydrochloric acid,	$\text{HCl}^{-}$
Hypochlorous acid,	$\text{HCl}^{\text{I}}\text{O}$
Chlorous acid,	$\text{HCl}^{\text{III}}\text{O}_2$
Chloric acid,	$\text{HCl}^{\text{V}}\text{O}_3$
Perchloric acid,	$\text{HCl}^{\text{VII}}\text{O}_4$

**834. Oxidation.**—*a.* The most delicate test for chlorine is potassium iodide with carbon disulphide. If, however, other oxidizing agents are present, the test must be varied to avoid error.

Chlorine is one of the strongest oxidizing agents, becoming always hydrochloric.

For action on  $\text{H}_2\text{C}_2\text{O}_4$ , see 659 ;  $\text{H}_3\text{PO}_2$ , 756 ;  $\text{H}_2\text{S}$ , 785 ;  $\text{H}_2\text{SO}_3$ , 813.

**HBr** *b.* Forms bromine and hydrochloric acid. In alkaline mixture forms an alkaline bromate.

**I** *c.* Forms iodic and hydrochloric acids. In presence of potassium hydroxide, potassium periodate is formed.

**HI** *d.* Forms first iodine, then iodic acid. With potassium hydroxide, same as above.

**HCNS** *e.* Forms first a red compound of unknown composition, then hydrocyanic, sulphuric, and hydrochloric acids.

$\text{H}_4\text{Fe}(\text{CN})_6$  *f.* Forms first ferricyanic and hydrochloric acids. Excess of chlorine to be avoided in preparation of ferricyanides.

$\text{H}_4\text{Fe}_2(\text{CN})_{12}$  *g.* Decomposes, forming various products.

*h.* Chlorine unites with all metals, forming chlorides. If any metal is capable of forming two series of salts, it always changes the one in which the metal has the less number of bonds, to that having the greater. That is, it changes *ous* salts to *ic*.

Especially in the presence of a fixed alkali, it changes nearly all the lower oxides and hydrates to the highest the metal is capable of forming. Among the ordinary metals, the only exceptions are peroxide of silver, and the peroxides of the alkalis and alkaline earths.

*i.* By comparing this with oxidation by **Br** and **I**, the following facts will be observed, and should be carefully considered. The elements chlorine, bromine, and iodine have an oxidizing power in order of their combining numbers, chlorine being the strongest. This rule has no exceptions.

Their hydric acids are reducing agents graded in the reverse order.

If any increase of bonds takes place in presence of an acid, by chlorine, bromine, or iodine, the same increase always occurs in presence of a fixed alkali. But the oxidation frequently goes further in presence of a fixed alkali. Thus, with chlo-

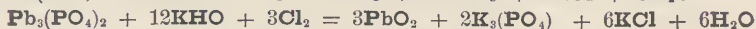
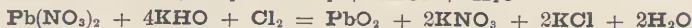


rine and potassium hydrate we form  $\text{PbO}_2$ ,  $\text{Ni}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_5$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{K}_2\text{FeO}_4$ , and  $\text{MnO}_2$ , which cannot be formed in presence of an acid.

It is very important to remember that *those oxides which are formed by chlorine, in presence of a fixed alkali, but not in presence of an acid, are the only ones which can be reduced by hydrochloric acid. And further, that this reduction proceeds not always to the original form, never proceeding beyond that number of bonds capable of being formed in presence of an acid.* Thus, any plumbic salt, with potassium hydroxide and chlorine, forms  $\text{PbO}_2$ , and this treated with hydrochloric acid again forms the plumbic salt,  $\text{PbCl}_2$ . And ferrous chloride with potassium hydroxide and chlorine forms  $\text{K}_2\text{FeO}_4$ , in which iron is a true hexad, and  $\text{K}_2\text{FeO}_4$  with hydrochloric acid forms, not the ferrous chloride with which we began, but ferric chloride, for it could be oxidized to that point in presence of an acid.

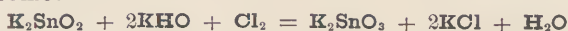
*The above rule is true for bromine and iodine, as well as for chlorine.*

**Pb'' j.** Becomes  $\text{PbO}_2$ , with fixed alkalis, not in acid solution.



**Hg'** *k.* Becomes  $\text{Hg}''$  in acid and in alkaline mixture.

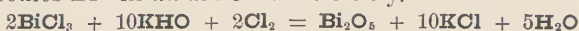
**Sn''** *l.* Becomes  $\text{Sn}''''$  " " "



**As'''** *m.* Becomes  $\text{As}^v$  in acid and alkaline mixture.

**Sb'''** *n.* Becomes  $\text{Sb}^v$  " " "

**Bi'''** *o.* Becomes  $\text{Bi}^v$  in alkaline mixture only.



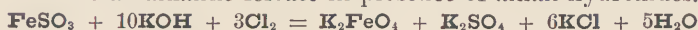
**Mn''** *p.* Becomes  $\text{MnO}_2$  in alkaline mixture only.

**Co''** *q.* Becomes  $\text{Co}_2(\text{OH})_6$  in alkaline mixture only.

**Ni''** *r.* Becomes  $\text{Ni}_2(\text{OH})_6$  " " "

**Cr'''** *s.* Becomes  $\text{Cr}^{vi}$  (a chromate) in alkaline mixture only.

**Fe''** *t.* Becomes  $\text{Fe}'''$  in alkaline and acid mixture, but is further oxidized to an alkaline ferrate in presence of alkali hydroxides.



#### HYDROCHLORIC ACID. $\text{HCl}$ .

835. Oxidation valence....  $\text{H}'\text{Cl}'$

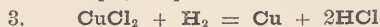
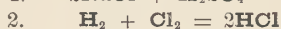
Structural valence....  $\text{H}-\text{Cl}$

The vapor density ( $\text{H} = 1$ ) is 18.185, showing that the molecule is  $\text{HCl}$ .

**HCl** gas under ordinary atmospheric pressure liquefies at  $-102^{\circ}$  C., and solidifies at  $-115.7^{\circ}$  C., melts again at  $-112.5^{\circ}$  C. (OLSZEWSKI, 1884). Under a pressure of 40 atmospheres it liquefies at  $10.6^{\circ}$  C. (MITCHELL).

**Occurrence.**—Not found native except in volcanic gases and in springs and rivers in the vicinity of volcanoes. Found as a chloride in many minerals, its most abundant source being sodium chloride.

**836. Preparation.**—(1) For commercial purposes always made by action of  $\text{H}_2\text{SO}_4$  on **NaCl**. Sulphuric displaces hydrochloric acid from all chlorides. Exception: It has no action on  $\text{Hg}_2\text{Cl}_2$  and  $\text{HgCl}_2$ , and the chlorides of silver, lead, and tin are but imperfectly transposed. (2) By direct combination of **H** and **Cl** by means of heat, light, or electricity. (3) The chlorides of the first two groups and of **Zn**, **Fe**, **Co**, and **Ni** are reduced to the metallic state when heated in hydrogen gas, **HCl** being evolved.



**837.** Absolute hydrochloric acid is a colorless, caustic, suffocating gas. It **dissolves** in about two parts by weight of water. At  $15^{\circ}$  C. a saturated solution having a specific gravity of 1.2124 contains 43.09 per cent. of **HCl** (J. KOLB, 1872). Its strongest permanent solution contains about 33 per cent. of acid (**HCl**); but this solution rapidly evolves acid in the air, more rapidly on warming, less rapidly as the solution loses strength. When of 20 per cent. acid, the liquid boils at  $112^{\circ}$  C. ( $233^{\circ}$  F.), vaporizing with the water of its solution. The U. S. P. acid contains 31.9 per cent. of **HCl**, and its sp. gr. is 1.16.

**838.** Gaseous hydrochloric acid escapes with slow **effervescence** when liberated from compounds in concentrated solution; reddens **litmus**; with vapor of **ammonia**, gives a white cloud ( $\text{NH}_4\text{Cl}$  as a solid), somewhat more dense than the fumes caused by the other volatile acids; and, like aqueous hydrochloric acid (842), precipitates chlorides from salts of the **first-group metals**, when brought in contact with their solutions—a drop adhering to a glass rod being held in the gas.

**839.** Hydrochloric acid is formed from metallic chlorides by transposition with **sulphuric acid**; except that silver, lead, and tin chlorides are transposed with difficulty, and mercurous and mercuric chlorides not at all, by sulphuric acid:



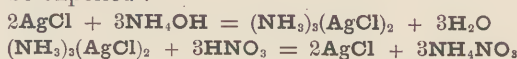
**840.** The normal *Chlorides* are all **soluble in water**, except those of the metals of the first group; silver, **AgCl**; mercurous,  $\text{Hg}_2\text{Cl}_2$ ; and lead, **PbCl}\_2**—the last named being sparingly soluble. In **analysis**, the silver precipitate is most used (843). If bromides are present, the chlorochromic test is most conclusive (845).

A large number of the metallic chlorides are soluble in alcohol, and several are soluble in ether.

841. The chlorides of metals are, generally, more **volatile** than other compounds of the same metals; example, ferric chloride.

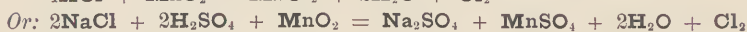
842. Solutions of chlorides and hydrochloric acid are precipitated, by solutions of **silver salts**, as *silver chloride*,  $\text{AgCl}$ , white (413); by solutions of **mercurous salts**, as *mercurous chloride*,  $\text{Hg}_2\text{Cl}_2$ , white (436); and by solutions of **lead salts**, when not very dilute, as *lead chloride*,  $\text{PbCl}_2$ , white (390). **Silver nitrate** solution is the most complete and convenient precipitant for chlorides. Exceptions:  $\text{HgCl}_2$  does not precipitate lead salts. The chlorine in green  $\text{Cr}_2\text{Cl}_6$  is incompletely precipitated by  $\text{AgNO}_3$  (PELLIGOT); whilst from a solution of oxychloride of molybdenum in  $\text{H}_2\text{SO}_4$  it is not precipitated at all (BLOMSTRAND).

843. The properties of the precipitate of *silver chloride* are given in 413 and in 409. It is of analytical interest that it is freely soluble in **ammonium hydroxide** (considerably more freely than the bromide, and far more freely than the iodide of silver); soluble in hot, concentrated solution of **ammonium carbonate** (which dissolves traces of bromide, and no iodide of silver); insoluble in nitric acid, or but temporarily soluble in strong nitric (as in hydrochloric) acid, and precipitating again on dilution. It should be observed, that it is appreciably soluble in solutions of chlorides, and in ammonium nitrate; hence, in reprecipitating traces of it, by nitric acid, from the ammonia solution, if there is excess of ammonium hydroxide, this should first be expelled:



844. Oxidizing agents (with heat) *decompose hydrochloric acid*.

The action of *manganese dioxide* is formulated as follows:

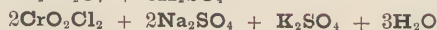
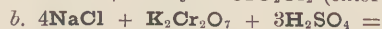
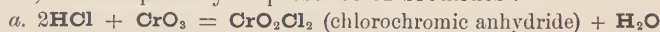


For more complete statement of the oxidation of  $\text{HCl}$  see 851.

This reaction is applied in the manufacture of chlorine, which is distilled from the mixture, and can be used in analysis for evidence of chlorides.

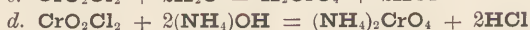
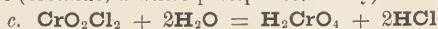
A test for *traces of free hydrochloric acid*, in distinction from metallic chlorides, is made by heating the solution with  $\text{MnO}_2$ , without adding an acid, and distilling into a solution of potassium iodide and starch. Larger proportions of  $\text{HCl}$  are more frequently separated by distilling it intact.

845. The reaction with *chromic anhydride* is in use as a test for hydrochloric acid, more especially in presence of bromides:

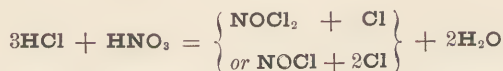


To obtain a rapid production of the gas, so that it may be recognized by its color, the operation may be made as follows: Boil a mixture of solid **potassium dichromate** and **sulphuric acid**, in an evaporating-dish until bright red, and then add the substance

to be tested, in powder—obtained, if necessary, by evaporation of the solution. If chlorides are present, the chromium dioxy-dichloride rises instantly as a bright brownish-red gas. The *distinction from bromine* requires, however, that the material, which may be in solution, should be *distilled*, by means of a tubulated flask or small retort, the vapors being condensed in a receiver, and neutralized with an alkali (*c* and *d*). The chromate formed makes a yellow solution (bromine, a colorless solution). As conclusive evidence of chlorine, the chromate (acidified with acetic acid), with lead acetate, forms a yellow precipitate (bromide, a white precipitate, if any):

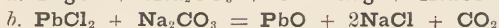
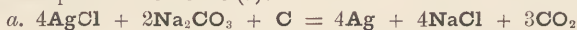


**846.** The action of *nitric acid* with hydrochloric acid results from the mixture of the two acids, well known as nitro-hydrochloric acid, or “aqua regia,” and used for its free chlorine. Both nitrogen oxychloride and nitrogen oxydichloride are formed; their relative proportion varying with different conditions:



The reaction occurs quite promptly in the concentrated acids without heat, but more rapidly with heat; very slowly in moderately dilute acids, and only to a slight extent if the acids are very dilute.

**847.** The *three chlorides insoluble* in water (840) are not transposed or dissolved by acids, except that mercurous chloride is dissolved, by nitric acid and by chlorine, as mercuric salt. They are dissolved for analysis by decomposition with **alkali hydroxides**. **AgCl** or **PbCl<sub>2</sub>** is dissolved as sodium chloride, after fusion with sodium carbonate on charcoal (*a*), or in a porcelain crucible (*b*):



**848.** Heated in a bead of microcosmic salt, previously saturated with copper oxide in the inner blow-pipe flame, chlorides impart a *blue color* to the outer flame, due to copper chloride.

**849. Estimation.**—(1) It is precipitated by **AgNO<sub>3</sub>**, washed, and, after ignition, weighed as **AgCl**. (2) By a standard solution of **AgNO<sub>3</sub>**. A little **Na<sub>2</sub>HPO<sub>4</sub>**, or, better, **K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>**, is added to the chloride to show the end of the reaction. When enough **AgNO<sub>3</sub>** has been added to combine with the chlorine the next addition gives a yellow precipitate with the phosphate, or a red with the chromate.

**850.** Chlorides may be made, *a*, by direct union of the elements, mostly without heat. Whether an *ous* or *ic* salt is formed depends upon the amount of chlorine used. *b*. By the action of hydrochloric acid upon the corresponding oxides, hydroxides, carbonates, or sulphites. The solutions formed may be evaporated to expel excess of acid. If the chlorides thus formed contain water of crystallization it cannot be removed by heat alone, for part of the acid is by this means driven off, and a basic salt remains. If the anhydrous chloride is desired, it may always be made by *a*, and when



thus formed may be sublimed without decomposition. *c.* Chlorides of the first group are best made by precipitation. Exception: *Mercuric* chloride does not precipitate *lead* salts. *d.* Metals soluble in hydrochloric acid evolve hydrogen and form chlorides. In these cases *ous*, and not *ic*, salts are formed.

*e.* Many chlorides may be formed by bringing  $\text{HgCl}_2$  in contact with the hot metal.

**851. Oxidation.**—For some properties of hydrochloric acid consult 834 *i.* For action on  $\text{HNO}_3$  see 846.

$\text{HClO}$  *a.* Forms chlorine and water.  $\text{HClO} + \text{HCl} = \text{Cl}_2 + \text{H}_2\text{O}$ .

$\text{HClO}_2$  *b.* Gives either free chlorine or a varying amount of the several oxides of chlorine [*Storer's Quantitative Analysis*, 119].

$\text{HBrO}_3$  *c.* Forms free bromine and chlorine.

$\text{HIO}_3$  *d.* In dilute solution, no action. If concentrated, yellow chloride of iodine,  $\text{ICl}_3$ , is formed, not taken up by carbon disulphide. On boiling, some free iodine is separated, which colors the carbon disulphide.

*e.* In all cases where metals are dissolved in hydrochloric acid, hydrogen is evolved. In such cases it is an oxidizing agent, the chlorine of the acid not changing its bonds, but the hydrogen is changed from combined, in which it is plus, to free hydrogen, where it has no bonds, thereby losing one bond. Or, as explained in 614,  $(\text{H}_2)^\circ = (\text{H}^+ \text{H}^-)^\circ$ .

For its action on oxides see 834 *i.*

$\text{Pb}_3\text{O}_4$  and  $\text{PbO}_2$  *f.* Form plumbic chloride and chlorine.

$\text{Mn}^{n+}$  *g.* Becomes  $\text{Mn}^{II}$  and  $(\text{Cl}_2)^\circ$  is formed. That is, all compounds of manganese having more than two bonds are reduced to the dyad, with evolution of chlorine. In case of dilute  $\text{K}_2\text{Mn}_2\text{O}_8$  this change is preceded by formation of manganese peroxide [*S. U. Pickering, Jour. Chem. Society*, 35, 654].

$\text{Co}^{III}$  and  $\text{Ni}^{III}$  *h.* Are changed to cobaltous and nickelous chlorides, with evolution of chlorine.

$\text{Fe}^{VI}$  *i.* With the exception of ferrates, as  $\text{K}_2\text{FeO}_4$ , which forms ferric chloride, the compounds of iron are not reduced.

$\text{Cr}^{VI}$ . Forms chromic chloride, and chlorine is evolved.

## HYPOCHLOROUS ACID. $\text{HClO}$ .

**852.** Oxidation valence..... $\text{H}^+\text{Cl}^{\text{O}-}$

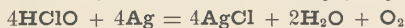
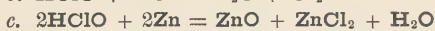
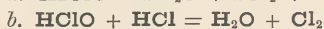
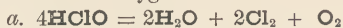
Structural valence..... $\text{H}-\text{O}-\text{Cl}$

Vapor density of the anhydride,  $\text{Cl}_2\text{O}$ , 43.5.

Hypochlorous *anhydride*.  $\text{Cl}_2\text{O}$ , can be obtained at  $-20^\circ \text{C}$ . ( $-4^\circ \text{F}$ .), by the reaction,  $\text{HgO} + 2\text{Cl}_2 = \text{Cl}_2\text{O} + \text{HgCl}_2$ , as an orange-colored, explosive liquid, *gaseous* at ordi-

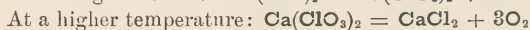
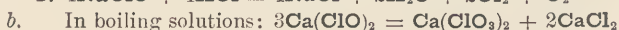
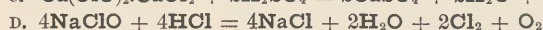
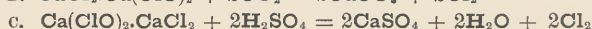
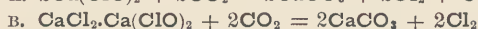
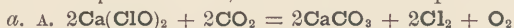
nary temperatures, and decomposing, spontaneously and sometimes violently, into chlorine and oxygen. It dissolves in water, forming hypochlorous acid,  $\text{HClO}$ .

Hypochlorous acid, in aqueous solution, is a yellow liquid; when strong, decomposing rapidly at  $0^\circ \text{C}$ . ( $32^\circ \text{F}$ .); when dilute, decomposing gradually by boiling (*a*); decomposed by hydrochloric acid (*b*), and by metals (*c*)—its decompositions furnishing chlorine or oxygen, or both chlorine and oxygen.



853. The **Hypochlorites** are formed by treating bases with chlorine (short of saturation), as shown in *b*, 833. The calcium hypochlorite and chloride, mixed or combined together as formed by action of chlorine upon calcium hydroxide, is in very extensive use—as chlorinated lime, or “chloride of lime” [ $\text{CaCl}_2 + \text{Ca}(\text{ClO})_2$ , or  $2\text{Ca}(\text{OCl})\text{Cl}$ ]. The sodium hypochlorite-and-chloride—mixed as formed by chlorine in solution of sodium hydrate or sodium carbonate, or by double decomposition between solution of the calcium hypochlorite-and-chloride and solution of sodium carbonate—is pharmacopœial, under the name of solution of chlorinated soda ( $\text{NaCl}.\text{NaClO}$ ). The chemical structure of these important chlorinated compounds has been difficult to ascertain.

854. Hypochlorites are very *instable*, whether solid or in solution, decomposing by the weakest acids, by the carbonic acid of the air (*a*), and by heat (*b*), also to some extent at ordinary temperatures. In this manner, they act as *powerful oxidizing agents*. The deportment of hypochlorites is represented by the action of *chlorine in alkali solutions* (833 *b*); a convenient agent of especial force, as for the decomposition of ammonia (45 *b*).



All hypochlorites are **soluble in water**; those of the first-group metals being especially instable. Their solutions bleach **litmus** and indigo.

**Silver nitrate**, added to the solutions of hypochlorites with chlorides, precipitates the chloride,  $\text{AgCl}$ , at first leaving hypochlorites in solution; while the soluble *silver hypochlorite* quite rapidly decomposes with the precipitation of chloride and formation of chlorate of silver (*a*), the latter slowly changing to chloride.



**Oxidation.**—The oxidizing power of this acid is, in general, the same as that of free chlorine.

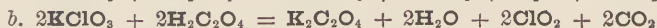
CHLOROUS ACID.  $\text{HClO}_2$ .855. Oxidation valence..... $\text{H}'\text{Cl}^{\text{III}}\text{O}^{\text{--}''}_2$ Structural valence..... $\text{H}-\text{O}-\text{Cl}=\text{O}$ Vapor density of the anhydride,  $\text{Cl}_2\text{O}_3$ , experimental ( $\text{H}=1$ ), 58.4.

The anhydride is prepared, according to Millon, by mixing 15 parts  $\text{As}_2\text{O}_3$ , 20 parts  $\text{KClO}_3$ , 60 parts  $\text{HNO}_3$ , sp. gr. 1.33, and 20 parts water; the temperature is cautiously kept at  $25^\circ$  to  $45^\circ$  C.; the  $\text{Cl}_2\text{O}_3$  gently distills over, and is received in a flask partly filled with water. It should be observed that the amount of  $\text{As}_2\text{O}_3$  taken is limited; a larger amount would reduce the  $\text{HClO}_3$  to  $\text{HCl}$ . Dilute  $\text{H}_2\text{SO}_4$  may be used instead of  $\text{HNO}_3$ , and instead of  $\text{As}_2\text{O}_3$  De Vry uses tartaric acid, Schiel uses cane sugar, and Carius uses benzene; in which cases  $\text{CO}_2$  is also formed. The greenish-yellow anhydride passed into water forms the reddish-brown acid, and by treating this with hydroxides a few salts have been prepared—*e.g.*,  $\text{KClO}_2$ ,  $\text{NaClO}_2$ ,  $\text{AgClO}_2$ ,  $\text{Pb}(\text{ClO}_2)_2$ ,  $\text{Ba}(\text{ClO}_2)_2$ ,  $\text{Sr}(\text{ClO}_2)_2$ . The anhydride explodes at  $57^\circ$  C., forming oxygen and chlorine. Most chlorites are soluble; silver chlorite sparingly. The acid decolors  $\text{K}_2\text{Mn}_2\text{O}_8$ , and bleaches indigo solution. If a slightly acidulated dilute solution of a ferrous salt is mixed with a dilute solution of chlorous acid, the liquid transiently acquires an amethyst tint, and does not assume the yellowish color of ferric salts until the lapse of a few seconds (LENSEN).

CHLORINE PEROXIDE.  $\text{ClO}_2$ .856. Oxidation valence..... $\text{Cl}^{\text{IV}}\text{O}^{\text{--}''}_2$ 

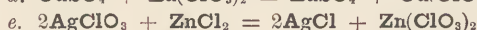
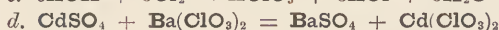
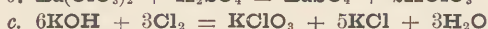
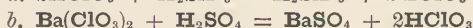
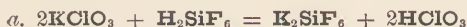
Structural valence....not satisfactorily determined.

Vapor density at  $30^\circ$  C. ( $\text{H}=1$ ) is 33.65. Made by the action of  $\text{H}_2\text{SO}_4$  (*a*) or  $\text{H}_2\text{C}_2\text{O}_4$  (*b*) upon  $\text{KClO}_3$ . It is a dark yellow gas, which condenses by cold to an orange-colored solid, which melts at  $-76^\circ$  C. (FARADAY), and under 730.9 m.m. pressure boils at  $9.9^\circ$  C. (SCHACHERL, 1881). It decomposes explosively by heat, light, or by contact with reducing agents, such as P, S, sugar, ether, and turpentine. Passed into  $\text{KOH}$  forms  $\text{KClO}_2$  and  $\text{KClO}_3$  (*c*) (MILLON).

CHLORIC ACID.  $\text{HClO}_3$ .Oxidation valence..... $\text{H}'\text{Cl}^{\text{V}}\text{O}^{\text{--}''}_3$ ,Structural valence..... $\text{H}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{Cl}}}=\text{O}$ 

857. Preparation.—From  $\text{KClO}_3$ , by adding  $\text{H}_2\text{SiF}_6$  (*a*). Or from  $\text{Ba}(\text{ClO}_3)_2$ , by adding exactly the required quantity of  $\text{H}_2\text{SO}_4$  (*b*). The

chlorates of the alkalis and alkaline earths are made by action of excess of chlorine upon a hot solution of the hydroxides (*c*). Other chlorates are formed by action of  $\text{Ba}(\text{ClO}_3)_2$  upon the respective sulphates (*d*), or of  $\text{AgClO}_3$  upon the respective chlorides (*e*). And all may be formed by action of the free acid upon the corresponding hydroxides or carbonates. The mercurous and ferrous salts are very instable, and those of antimony, tin, bismuth, and manganese are not with certainty known. The anhydride,  $\text{Cl}_2\text{O}_5$ , has not been isolated.



**858. Properties.**—The aqueous solution may be concentrated in a vacuum until its sp. gr. is 1.282 and contains 40.1 per cent. of  $\text{HClO}_3$ . It is a colorless, syrupy liquid, having a slight odor, resembling nitric acid. It first reddens litmus, and then bleaches it. Chloric acid is somewhat instable at ordinary temperatures; when heated, it rapidly decomposes with formation of yellow products, including perchloric acid ( $\text{HClO}_4$ ), chlorine and water. It oxidizes organic and other combustible substances with violent rapidity.

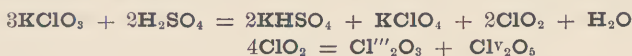
All chlorates are resolved by heat into chlorides and oxygen ( $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$ ). In presence of various metallic oxides, etc., the oxygen is separated more easily, the metallic oxides remaining unchanged. With manganese dioxide, the oxygen of potassium chlorate is obtained at about  $200^\circ \text{C}$ .; ferric oxide, at  $120^\circ \text{C}$ .; platinum, black, at  $270^\circ$ . Copper oxide and lead dioxide may be used. When *trituated or heated* with **combustible substances**, charcoal, organic substances, sulphur, sulphites, cyanides, thiosulphates, hypophosphites, reduced iron, etc., etc.—*chlorates violently explode*, owing to their sudden decomposition, and the simultaneous oxidation of the combustible material. This explosion is more violent than with corresponding mixtures of nitrates (as in gunpowder, 730).

**859.** All the chlorates are **soluble in water**; those of the first-group bases being somewhat instable in solution. Like nitric and acetic acids, chloric acid is *not precipitated*. Except the mercurous, the least soluble of the metallic chlorates is that of potassium, which requires 12 to 16 parts of cold water for its solution. Potassium chlorate is only slightly soluble in alcohol. Chlorates are usually **identified** by the gaseous products of decomposition (860).

**860.** Sulphuric acid causes dissociation of chlorates—if in the solid state, with *detonation*, and, unless in small quantities, with violent explosion; and with formation of *greenish-yellow gas*, chlorine peroxide. Perchlorate is likewise formed. The gas has the odor, oxidizing and bleaching

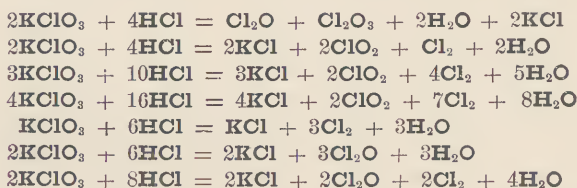


power of chlorine, and it imparts its color to solutions in which it is formed. The products vary with conditions, but are chiefly formed as follows :



If a dilute solution of a chlorate is colored light blue with the solution of indigo in sulphuric acid, and the solution kept cold, no bleaching occurs, even with the further addition of dilute sulphuric acid. But, on addition of solution of sodium sulphite, the color soon disappears, by formation of chlorine or its oxides.

**861. Hydrochloric acid** decomposes chlorates, rapidly when heated, with the formation of free *chlorine* and chlorine peroxide—the mixture called *euchlorine*. The gas and solution have the color, odor, and bleaching effect of chlorine, intensified. This is a ready and effective means of generating chlorine for analytical purposes. The proportion of free chlorine to oxidized chlorine is variable, the subjoined equations showing the character of the results. According to Bunsen, sometimes only free chlorine is produced; at others, only  $\text{Cl}_2\text{O}$ ; at others, both gases are evolved, and occasionally  $\text{Cl}_2\text{O}_3$  is formed.



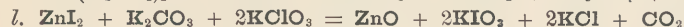
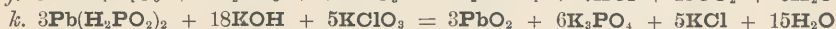
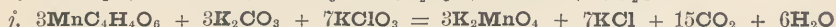
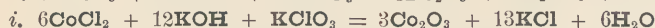
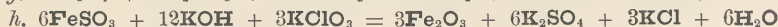
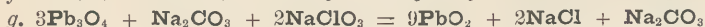
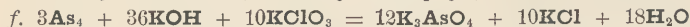
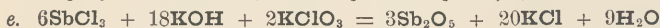
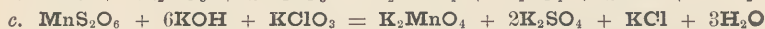
If a solution of a chlorate be acidified with dilute sulphuric acid, and **zinc** added, the liberated chloric acid is reduced to hydrochloric acid by the nascent hydrogen. If a dilute solution of an alkaline chlorate is boiled with a **copper-zinc couple**,\* it is completely reduced to chloride with separation of oxide of zinc (THORPE and ECCLES).

Chloric acid behaves like nitric acid with **brucine** (LUCK), **diphenylamine**, **paratoluidine**, and **phenol**, dissolved in concentrated sulphuric acid, or at all events the reactions are so similar that the two acids cannot be distinguished with certainty by these reagents. Chloric may, however, be distinguished from nitric acid by its action on phenol in hydrochloric acid solution (compare 728), inasmuch as the chloric acid produces an orange-red turbidity.

**862. Estimation.**—(1) Reduce the chlorate to a chloride by dilute  $\text{H}_2\text{SO}_4$  and **Zn**, or if it is an alkaline chlorate, by fusion. It may then be estimated as a chloride. (2) Add **HCl** and **KI**, and determine the liberated iodine by standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$ . Which of the products of decomposition given above may actually be formed, whether all or only certain of them, cannot be foreseen. But no matter which of them may be formed, they all of them agree in this, that, in contact with solution of potassium iodide, they liberate 6 atoms of iodine for every molecule of  $\text{HClO}_3$ .

\* Gladstone and Tribe's copper-zinc couple is prepared by treating thin zinc foil with a 1 per cent. solution of copper sulphate until the zinc is covered with a black deposit of reduced copper. When washed and dried it is ready for use.

**863. Oxidation.**—Alkali chlorates when fused with an alkali, or an alkali carbonate, and a free metal or a lower oxide, or salt of the metal, generally oxidizes it to a higher oxide, or to a salt having an increased number of bonds; and the chlorate is reduced to a chloride—*e.g.*,  $\text{Mn}^{\text{vi}} - n$  becomes  $\text{Mn}^{\text{vi}}$ . That is, any compound of manganese having less than six bonds is oxidized to the hexad (*a*). In equations (*b*) and (*c*) the sulphur is also oxidized.  $\text{Cr}^{\text{iii}}$  becomes  $\text{Cr}^{\text{vi}}$  (*d*).  $\text{Sb}^{\text{v}} - n$  becomes  $\text{Sb}^{\text{v}}$  (*e*).  $\text{As}^{\text{v}} - n$  becomes  $\text{As}^{\text{v}}$  (*f*).  $\text{Pb}^{\text{iv}} - n$  becomes  $\text{Pb}^{\text{iv}}$  (*g*).  $\text{Fe}^{\text{iii}} - n$  becomes  $\text{Fe}^{\text{iii}}$  (*h*).  $\text{Co}^{\text{iii}} - n$  becomes  $\text{Co}^{\text{iii}}$  (*i*). Also  $\text{C}^{\text{iv}} - n$  becomes  $\text{C}^{\text{iv}}$  (*j*).  $\text{P}^{\text{v}} - n$  becomes  $\text{P}^{\text{v}}$  (*k*).  $\text{I}^{\text{v}} - n$  becomes  $\text{I}^{\text{v}}$  (*l*).  $\text{S}^{\text{vi}} - n$  becomes  $\text{S}^{\text{vi}}$  (*m*).



Free chloric acid is a strong oxidizing agent, and if an excess of the reducing agent is used, it is converted into  $\text{HCl}$ , or a chloride, but if heat be employed the chloric acid splits up and some free chlorine, or its oxides, may be formed. For its action on acids already given, see  $\text{H}_2\text{C}_2\text{O}_4$ , 659;  $\text{H}_3\text{PO}_3$ , 756;  $\text{HCNS}$ , 702;  $\text{H}_4\text{Fe}(\text{CN})_6$ , 691;  $\text{H}_6\text{Fe}_2(\text{CN})_{12}$ , 694;  $\text{H}_2\text{S}$ , 785;  $\text{H}_2\text{SO}_3$ , 813;  $\text{HCl}$ , 861.

$\text{HBr}$  *a.* Forms bromine.

$\text{I}$  *b.* Forms  $\text{HIO}_3$ .

$\text{HI}$  *c.* Forms first  $\text{I}^\circ$  then  $\text{I}^{\text{v}}$  (free iodine and iodic acid).

$\text{Hg}'$  *d.* Forms  $\text{Hg}''$ .

$\text{Sn}''$  *e.* Forms  $\text{Sn}^{\text{iv}}$ .

$\text{Sb}'''$  *f.* Forms  $\text{Sb}^{\text{v}}$ .

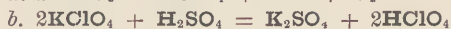
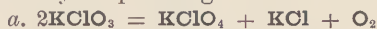
$\text{As}'''$  *g.* Forms  $\text{As}^{\text{v}}$ .

$\text{Fe}''$  *h.* Forms  $\text{Fe}'''$ .

$\text{Cu}'$  *i.* Forms  $\text{Cu}''$ .

PERCHLORIC ACID.  $\text{HClO}_4$ .Oxidation valence..... $\text{H}^{\text{Cl}^{\text{VII}}\text{O}^{-1}}_4$ Structural valence..... $\text{H}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{Cl}=\text{O}$ 

864. Potassium perchlorate is first formed by heating  $\text{KClO}_3$  to about  $350^\circ \text{C}$ . (a), and, after separating the chloride by washing, it is treated with concentrated  $\text{H}_2\text{SO}_4$  and distilled, the  $\text{HClO}_4$  passing into the receiver (b). Or it may be made by evaporating a solution of chloric acid (c).



The pure perchloric acid is a colorless, very heavy liquid (sp. gr. 1.782), which soon becomes yellow from decomposition. It cannot be kept for any length of time. When heated, it undergoes decomposition, often with explosion. In its oxidizing properties it is more powerful than chloric acid. It burns the skin in a very serious manner, and sets fire to paper, charcoal, etc., with explosive violence. This want of stability, however, belongs only to the pure acid. If water be added to it heat is evolved, and a dilute acid of a far greater permanence is obtained. Diluted perchloric acid does not even bleach, but reddens litmus in the ordinary way.

Hydrochloric acid, nitric acid, and sulphurous acid do not decompose aqueous solutions of perchloric acid or perchlorates; solution of indigo, therefore, previously added to it, is not decolorized (difference from all other acids of chlorine). The alkaline perchlorates are not reduced by the copper-zinc couple (distinction from chloric acid, 861).

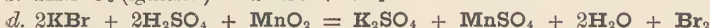
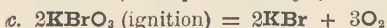
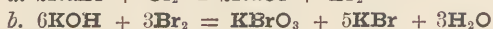
All the metallic perchlorates are soluble in water; potassium perchlorate requiring 58 parts (rubidium perchlorate, 92 parts) of water at  $21^\circ \text{C}$ ., the other metals forming salts more freely soluble. The potassium salt is insoluble in alcohol. In *ignition*, perchlorates act very much like chlorates, but more explosively.

BROMINE.  $\text{Br} = 79.768$ .Oxidation valence of free bromine..... $(\text{Br}_2)^\circ$ Structural valence of free bromine..... $\text{Br}-\text{Br}$ 

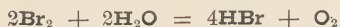
865. The vapor density at  $100^\circ \text{C}$ . ( $\text{H} = 1$ ) is 80, showing that the molecule is  $\text{Br}_2$ , but at  $1570^\circ \text{C}$ . (MEYER and ZUBLIN, *Berichte*, 13, 405) it is 53.33, which would make the molecule about  $\frac{2}{3}\text{Br}_2$ , the molecules undergoing partial dissociation into atoms. Solidifies at  $-7.2^\circ \text{C}$ . (PHILIPP, 1879). Boiling point,  $59.27^\circ \text{C}$ . (THORPE, 1880).

**Occurrence.**—It is never found free, but usually as a bromide of **K**, **Na**, or **Mg**. Found in sea-water, sea-weeds, and salt springs.

**Preparation.**—(1) The mother-liquor from the salt wells is condensed by evaporation, and the greater portion of the **NaCl**, **Na<sub>2</sub>SO<sub>4</sub>**, **MgSO<sub>4</sub>** is separated by crystallization. By the *old method* the **NaBr** is then treated with chlorine (*a*), an excess of chlorine being avoided, which would form bromine chloride. The solution is then shaken up with ether, which absorbs the bromine. Then the ether solution is shaken with solution of **KOH**, which forms **KBr** and **KBrO<sub>3</sub>** (*b*). The ether is separated and is used again for the same purpose. The mixed **KBr** and **KBrO<sub>3</sub>** is then ignited (*c*). It is then distilled with **MnO<sub>2</sub>** and **H<sub>2</sub>SO<sub>4</sub>** (*d*). If any iodine is present it is removed by precipitation as euprous iodide, and the last traces of chlorine are removed by adding **KBr** and redistilling (compare *a*). If the anhydrous bromide is required it is distilled from fused **CaCl<sub>2</sub>**. (2) A later method is to add the necessary **MnO<sub>2</sub>** and **H<sub>2</sub>SO<sub>4</sub>** directly to the mother-liquor and distill off the bromine. The use of ether is omitted, **KOH** or **NaOH** is added to the distillate, which is then treated as in (1).



**866. BROMINE**, at ordinary temperatures, is a brown-red, intensely caustic liquid, freely evolving brown-red, corrosive vapors of a suffocating, chlorine-like odor, and boiling at 47° C. (117° F.) It is soluble in 33 parts of water, with an orange-yellow color; and freely soluble in alcohol, ether, chloroform, and in carbon disulphide—with the same or a deeper color. Carbon disulphide, and chloroform, after agitation with its dilute water solutions, remove the bromine as a subsiding liquid in a yellow to red-brown layer; ether, less perfectly, in a supernatant layer of the same color. It dissolves colorless in alkali hydroxides, with combination, forming bromides and bromates. The change corresponds exactly to that of chlorine, as shown in equation *b*, 833, and 865 *b*. It dissolves, without combination or loss of color, in solutions of hydrobromic acid, and of bromides. Its water solution is permanent, but sunlight decomposes it thus:



In vapor or solution, bromine bleaches litmus and indigo; colors starch-paste yellow; precipitates silver salts, yellow-white, bromide and bromate (as by equation *c*, 833); and lead salts, white. Bromine decomposes hydrosulphuric acid with separation of sulphur, and subsequent production of sulphuric acid; changes ferrous to ferric salts, and (in presence of water) acts as a strong oxidizing agent. It displaces iodine from iodides, and is displaced from bromides by chlorine; its character being intermediate between that of chlorine and that of iodine.



The Acids of Bromine are :

Hydrobromic acid,  $\text{HBr}'$ .

Hypobromous acid,  $\text{HBr}'\text{O}$ .

Bromic acid,  $\text{HBr}^{\text{v}}\text{O}_3$ .

**867. Estimation.**—(1) The bromine is made to act upon  $\text{KI}$ , and the iodine which is liberated is estimated by standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$ . (2) It is estimated by the amount of  $\text{As}_2\text{O}_3$  which it oxidizes in alkaline solution. (3) It is converted into  $\text{KBr}$  by  $\text{H}_2\text{S}$  or  $\text{H}_2\text{SO}_3$ , and then precipitated by  $\text{AgNO}_3$ , and weighed as  $\text{AgBr}$ .

**868. Oxidation.**—Bromine as an oxidizing agent is intermediate in strength between chlorine and iodine. In presence of acids it never acts as a reducing agent. In oxidizing it becomes  $\text{Br}'$ ; that is, hydrobromic acid or a bromide. For its action upon  $\text{H}_2\text{C}_2\text{O}_4$ , see 659;  $\text{H}_3\text{PO}_2$ , 756;  $\text{H}_2\text{S}$ , 785;  $\text{H}_2\text{SO}_3$ , 813;  $\text{Cl}$ , 834;  $\text{HCNS}$ , 702;  $\text{H}_4\text{Fe}(\text{CN})_6$ , 691.

$\text{S}^{\text{vi}} - n$  a. Becomes  $\text{S}^{\text{vi}}$  in alkaline and acid mixture.

$\text{HI}$  b. Forms  $\text{I}^{\circ}$  and  $\text{HBr}$ . In presence of alkali hydroxides, forms a bromide and iodate

$\text{Pb}''$  and  $\text{Pb}_3\text{O}_4$  c. In alkali mixture become  $\text{PbO}_2$ .

$\text{Hg}'' - n$  d. Forms  $\text{Hg}''$  in alkaline and acid mixture. That is, both metallic mercury and mercurous compounds are oxidized to mercuric compounds.

$\text{As}^{\text{v}} - n$  e. Forms  $\text{As}^{\text{v}}$  in alkaline and acid mixture. That is, free arsenic [ $\text{As}^{\circ}$  or  $(\text{As}_4)^{\circ}$ ] and the triad arsenic are changed to the pentad.

$\text{Sb}^{\text{v}} - n$  f. Forms  $\text{Sb}^{\text{v}}$  in alkaline and acid mixture.

$\text{Sn}^{\text{iv}} - n$  g. Becomes  $\text{Sn}^{\text{iv}}$  in alkaline and acid mixture.

$\text{Mn}^{\text{iv}} - n$  h. Becomes  $\text{Mn}^{\text{iv}}$  with alkalies, not with strong acids.

$\text{Cr}'''$  i. Becomes  $\text{Cr}^{\text{vi}}$  " " "

$\text{Ni}''$  j. Becomes  $\text{Ni}'''$  " " "

$\text{Co}''$  and  $\text{Co}_3\text{O}_4$  k. Becomes  $\text{Co}'''$  with alkalies, not with strong acids.

$\text{Fe}''' - n$  l. In acid mixture becomes  $\text{Fe}'''$ .

$\text{Fe}^{\text{vi}} - n$  m. In alkaline mixture becomes  $\text{Fe}^{\text{vi}}$  (a ferrate).

## HYDROBROMIC ACID. $\text{HBr}$ .

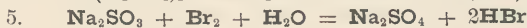
Oxidation valence..... $\text{H}'\text{Br}'$

Structural valence..... $\text{H}-\text{Br}$

**869.** Vapor density ( $\text{H} = 1$ ), 39.1. Condenses to a liquid at  $-69^{\circ}\text{C}$ ., and solidifies at  $-73^{\circ}\text{C}$ . (FARADAY).

**Preparation.**—Bromine does not combine with hydrogen, even in the sunlight; but if the mixed gases are passed over hot platinum sponge, combination results. It is prepared: (1) By action of  $\text{Br}$  on  $\text{P}$  and subsequent

distillation. Either variety of **P** will answer, but the amorphous is safer. (2) By adding  $\text{H}_3\text{PO}_4$  to **KBr** and distilling, precautions being taken to prevent bumping. (3) By distilling two parts of  $\text{CaBr}_2$ , two parts  $\text{H}_2\text{SO}_4$ , and one part  $\text{H}_2\text{O}$  (BERTRAND, 1876). (4) By action of **Br** on  $\text{H}_3\text{PO}_2$  or on  $\text{Ca}(\text{H}_2\text{PO}_2)_2$  and distilling. (5) By action of **Br** on  $\text{Na}_2\text{SO}_3$ . (6) By heating **Br** with paraffine, **HBr** distills over and the residue is chiefly carbon. (7) By adding to  $\text{BaBr}_2$  exactly enough  $\text{H}_2\text{SO}_4$  and decanting. (8) If made by action of  $\text{H}_2\text{SO}_4$  on **KBr** it generally contains free bromine. (9) By adding  $\text{H}_2\text{S}$  to the bromides of the first and second group metals. (10) By adding **Br** to an excess of  $\text{H}_2\text{S}$  solution, and removing  $\text{H}_2\text{SO}_4$ , if any be produced, by adding  $\text{Ba}(\text{OH})_2$  or  $\text{BaCO}_3$  and distilling.



**870 Properties.**—**HBr** is a colorless gas, fuming in moist air and having a very irritating odor. Its aqueous solution is colorless and not decomposed by exposure to the air. Water saturated at  $0^\circ \text{C}$ . contains 82.02 per cent. of **HBr**, and its sp. gr. is 1.78, very nearly  $\text{HBr} \cdot \text{H}_2\text{O}$  (BINEAU). If a saturated solution is boiled, chiefly **HBr** is given off, and if a dilute solution is boiled, chiefly  $\text{H}_2\text{O}$  is given off, until in both cases the remaining liquid contains 47.38 to 47.86 per cent. of **HBr**, its sp. gr. 1.485, its boiling point constant at  $126^\circ \text{C}$ ., and its composition almost exactly  $\text{HBr} \cdot 5\text{H}_2\text{O}$ , which distills over unchanged. Its vapor density of 14.1 agrees with the calculated vapor density of  $\text{HBr} \cdot 5\text{H}_2\text{O}$ .

**871.** The **solubilities** of the bromides lie intermediate between those of the chlorides and those of the iodides, not differing much from the former. In general terms, all *bromides are soluble in water, except those of the first-group bases*. Further, mercuric bromide is only sparingly soluble in water. Lead bromide is less soluble than lead chloride. Bismuth bromide is decomposed by water, to a greater extent than bismuth chloride (364), and antimonious bromide is decomposed by water. Cuprous bromide is formed as a precipitate by reduction from the soluble cupric bromide.

The *double bromides* of lead and potassium or sodium, and of silver and potassium or sodium, are soluble in a little water containing alkali bromides as concentrated solutions, but are decomposed by much water; the potassio and the sodio mercurous and mercuric bromides are soluble in water.

In *alcohol*, the alkali bromides are sparingly or slightly soluble; calcium bromide, soluble; mercuric bromide, soluble; mercurous bromide, insoluble.

*Silver* bromide is sparingly soluble in *ammonium hydroxide*; nearly insoluble in ammonium carbonate solution.

In **analysis**, bromides are usually identified by the color of a carbon-

disulphide solution of free bromine, iodine, if present, being first removed (873).

**872. Silver nitrate** solution precipitates, from solutions of bromides, *silver bromide*,  $\text{AgBr}$ , yellowish-white in the light, slowly becoming gray to black. The precipitate is insoluble in, and not decomposed by, nitric acid, sparingly soluble in concentrated aqueous ammonia, nearly insoluble in concentrated solution of ammonium carbonate, slightly soluble in excess of alkali bromides, soluble in solutions of alkali cyanides and thiosulphates. It is decomposed by chlorine.

Solution of **mercurous nitrate** precipitates *mercurous bromide*,  $\text{Hg}_2\text{Br}_2$ , yellowish-white, soluble in excess of alkali bromides.

Solutions of **lead salts** precipitate, from solutions not very dilute, *lead bromide*,  $\text{PbBr}_2$ , white (391 and 871).

**873. Sulphuric acid** decomposes all bromides, except those of silver and mercury: when dilute, mostly with production of hydrobromic acid; when concentrated, chiefly with formation of **bromine**. The vapor from the hot mixture reddens or bleaches *litmus*; has the yellowish-brown *color* and suffocating *odor* of bromine, and when cooled colors **starch-paste** yellow.

**Chlorine-Water** separates the bromine much more quickly and completely, giving better results in dilute solutions, but in excess it decolors the bromized starch.

The more delicate test is made by adding **carbon disulphide**,\* then dilute chlorine-water, drop by drop, in the cold solution; then agitating, and allowing the heavier liquid to subside (866). The presence of bromine is indicated by a *yellow* color, or if there is much bromine a yellowish-brown to brownish-red color. Iodine colors violet. *If free iodine is present*, bromine cannot be identified, by its vapor, its color with starch, or its color in solution with carbon disulphide. All the iodine of iodides will be liberated before any of the bromine can be: therefore, before these tests can be made for bromine, the iodine must either be oxidized to iodic acid, or wholly expelled.

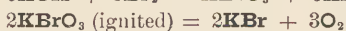
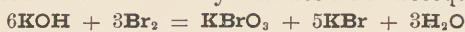
**Dilute hydrochloric acid** will not color dilute solutions of bromides, or, *in absence of oxidizing agents*, yield color to disulphide of carbon.

Bromides of potassium, sodium, and of most other metals, are not decomposed by **ignition**. Silver bromide melts undecomposed; but is slowly reduced, and blackened, in the air and by light.

Tested in the cupric bead, according to 848, bromides give a greenish-blue color to the outer flame—not very marked.

\* *Carbon disulphide* is a better color solvent, for bromine or iodine, than chloroform, and far better than ether. It must be free from sulphurous or sulphuric acids. Saturated chlorine-water is liable to act on carbon disulphide, giving it a yellow color, simulating bromine. On adding alcohol to this yellow liquid sulphur precipitates. Hence the direction to use dilute chlorine-water, and avoid excess.

**874.** Metallic bromides are formed : (1) By direct union of the elements, but in a few cases heat is required to effect the combination. (2) By action of **HBr** upon the metallic oxides, hydroxides, and carbonates. (3) Many bromides are formed by action of **HBr** on the free metal, *ous* salts and not *ic* being formed. (4) Bromides of the first group are best made by precipitation. (5) Bromides of **K**, **Na**, **Ba**, **Si**, and **Ca** are made by the action of bromine on their hydroxides and subsequent fusion.



**875. Estimation.**—Gravimetrically, it is precipitated by **AgNO<sub>3</sub>**, and, after ignition, weighed as **AgBr**. (2) Volumetrically (in same manner as **HCl**) by standard solution of **AgNO<sub>3</sub>**, using **K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>** to show when the reaction is complete. (3) It may be oxidized to free bromine and estimated as in 867.

**876. Oxidation.**—*a.* The bromine of **HBr** can never act as an oxidizing agent, for the reason that it is already reduced to its very lowest state of oxidation. When zinc is oxidized by **HBr** the change in bonds may be expressed thus :  $\text{Zn}^\circ + 2\text{H}'\text{Br}' = \text{Zn}''\text{Br}^{-1}_2 + (\text{H}_2)^\circ$ . That is, the zinc gains the two bonds lost by the two atoms of hydrogen, and the bonds of the bromine remain unchanged. When **HBr** acts as a reducing agent free bromine is formed, except that in alkaline mixture a bromate is produced.

**H<sub>2</sub>SO<sub>4</sub>** *b.* Dilute, no action ; concentrated becomes **SO<sub>2</sub>**.

**Cl** *c.* In acid mixture forms **HCl** and **Br<sup>o</sup>**, but in alkaline mixture forms a chloride and bromate.

**HClO** *e.* Same as free chlorine.

**HClO<sub>3</sub>** *f.* Forms chiefly **HCl**.

**HBrO<sub>3</sub>** *g.* Both acids are changed to free bromine.

**HIO<sub>3</sub>** *h.* Forms **I<sup>o</sup>** and **Br<sup>o</sup>** (free iodine and free bromine).

**Pb'' + n** *i.* Becomes **Pb''**.

**Sb<sup>v</sup>** *j.* Becomes **Sb'''**.

**Bi<sup>v</sup>** *k.* Becomes **Bi'''**.

**Mn'' + n** *l.* Becomes **Mn''**.

**Co'''** *m.* Becomes **Co''**.

**Ni'''** *n.* Becomes **Ni''**.

**Cr<sup>vi</sup>** *o.* Becomes **Cr'''**.

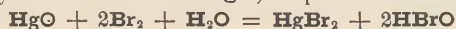
**Fe<sup>vi</sup>** *p.* Becomes **Fe'''**.

### HYPOBROMOUS ACID. **HBrO**.

Oxidation valence.....**H'Br'O''**

Structural valence.....**H-O-Br**

**877.** The anhydride, **Br<sub>2</sub>O**, has not been isolated. A solution of the acid is obtained by action of **Br** on **HgO**, in presence of **H<sub>2</sub>O**.





On warming, the  $\text{HBrO}$  is decomposed at  $60^\circ \text{C}$ . But it may be distilled unchanged in a vacuum at  $40^\circ \text{C}$ .  $\text{HBrO}$  is also formed by action of  $\text{Br}$  on  $\text{Ag}_2\text{O}$  or on  $\text{AgNO}_3$ . The hypobromites of  $\text{K}$ ,  $\text{Na}$ ,  $\text{Ba}$ ,  $\text{Ca}$ ,  $\text{Sr}$  may be formed by adding  $\text{Br}$  to an excess of the cold hydroxides. Aqueous  $\text{HBrO}$  is a yellow liquid, very instable, and a strong oxidizing and bleaching agent. The hypobromites are more instable than the corresponding hypochlorites.

### BROMIC ACID. $\text{HBrO}_3$ .

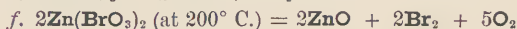
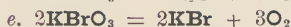
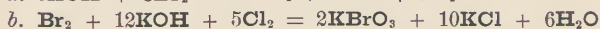
Oxidation valence..... $\text{H}^+\text{Br}^{\text{v}}\text{O}^{-''}$ ,

Structural valence..... $\text{H}-\text{O}-\overset{\text{O}}{\underset{|}{\text{Br}}}=\text{O}$

**878.** The anhydride,  $\text{Br}_2\text{O}_3$ , has not been isolated, and the acid,  $\text{HBrO}_3$ , is known only in solution. The bromates of  $\text{K}$ ,  $\text{Na}$ ,  $\text{Ba}$ ,  $\text{Sr}$ , and  $\text{Ca}$  are made by action of  $\text{Br}$  on the hot hydroxides (*a*); also by treating  $\text{Br}$  with  $\text{Cl}$  in presence of the hydroxides (*b*), and separating it from the bromide either by alcohol or recrystallizing. The remaining bromates may be made by adding bromic acid to the hydroxides or carbonates. Those of the first group and a few others are best made by precipitation. Free bromic acid may be made by action of  $\text{Br}$  on  $\text{AgBrO}_3$  (*c*), or by adding exactly enough  $\text{H}_2\text{SO}_4$  to  $\text{Ba}(\text{BrO}_3)_2$ .

**879. Properties.**—It may be concentrated in a vacuum until it contains 50.59 per cent.  $\text{HBrO}_3$ . Under ordinary atmospheric pressure decomposition begins when the liquid contains 4.27 per cent.  $\text{HBrO}_3$ ;  $\text{Br}$ ,  $\text{O}$ , and  $\text{H}_2\text{O}$  being formed (*d*).

The bromates are all decomposed by heat, some forming a bromide and  $\text{O}$ —*e.g.*, the bromates of the alkalies,  $\text{Hg}$ , and  $\text{Ag}$  (*e*). Some forming an oxide and  $\text{Br}$ —*e.g.*, bromates of  $\text{Mg}$ ,  $\text{Al}$ , and  $\text{Zn}$  (*f*). Others a mixed oxide and bromide—*e.g.*, bromates of  $\text{Pb}$ ,  $\text{Cu}$ , etc. When fused with reducing agents bromates explode like chlorates.



**880.** All the bromates are soluble in water; those of the first-group bases but sparingly soluble. Silver nitrate precipitates, in solutions not very dilute, silver bromate,  $\text{AgBrO}_3$ , white, very sparingly soluble in water, soluble in ammonium hydroxide, not easily soluble by nitric acid, its color and solubility in ammonium hydroxide differing a little from the bromide (872). It is decomposed by hydrochloric acid with evolution of bromine—a distinction from bromides and from other argentic precipitates.

**881.** Sulphuric, hydrochloric, and nitric acids liberate bromic acid from metallic bromates. With very **dilute sulphuric acid**, in cold dilute solution of pure bromate, very little bromine is set free—the  $\text{HBrO}_3$  mostly remaining for some time intact, and the solution colorless, so that carbon disulphide will not extract much color. The gradual decomposition of the  $\text{HBrO}_3$  is first a resolution into  $\text{HBr}$  and  $\text{O}$ , and as fast as  $\text{HBr}$  is formed it acts with  $\text{HBrO}_3$ , so as to liberate the bromine of both acids. Now, if the solution contained bromide as well as bromate, an abundance of free bromine is obtained *immediately* upon the addition of dilute sulphuric acid in the cold.

**882.** Hence, if dilute sulphuric acid in the dilute cold solution does not color the carbon disulphide, and if the addition of solution of pure potassium **bromide** immediately develops the yellow color, while it is found that no other oxidizing agent is present, we have corroborative evidence of the presence of a bromate. And, if we treat a solution known to contain bromide with dilute sulphuric acid and carbon disulphide, and obtain no color, we have conclusive evidence of the *absence* of bromates.

A mixture of *bromate and iodate*, treated with **hydrochloric acid**, furnishes bromine without iodine, coloring carbon disulphide yellow.

The ignited residue of bromates (879), in all cases if the ignition be done with sodium carbonate, will give the tests for bromides.

**883. Oxidation.**—*a.* When bromic acid is reduced an excess of the reducing agent usually produces  $\text{HBr}$  or a bromide. But with a few reducing agents only free bromine is formed. *b.* For action upon  $\text{H}_2\text{C}_2\text{O}_4$  see 659;  $\text{HCNS}$ , 702;  $\text{H}_4\text{Fe}(\text{CN})_6$ , 691;  $\text{H}_3\text{PO}_2$ , 756;  $\text{H}_2\text{S}$ , 785;  $\text{H}_2\text{SO}_3$ , 813;  $\text{HCl}$ , 851;  $\text{HBr}$ , 876.

**HI** *c.* Forms  $\text{Br}^\circ$  and  $\text{I}^\circ$ .

**Hg'** *d.* Becomes  $\text{Hg}''$  and  $\text{Br}'$  (a bromide).

**Sn''** *e.* Becomes  $\text{Sn}^{\text{IV}}$  and  $\text{Br}'$ .

**Sb'''** *f.* Becomes  $\text{Sb}^{\text{v}}$  and  $\text{Br}'$ .

**Fe''** *g.* Becomes  $\text{Fe}'''$  and  $\text{Br}'$ .

**As'''** *h.* Becomes  $\text{As}^{\text{v}}$  and  $\text{Br}'$  ( $\text{HBr}$ ).

## IODINE. $\text{I} = 126.557$ .

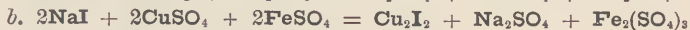
Oxidation valence of free iodine..... $(\text{I}_2)^\circ$

Structural valence of free iodine..... $\text{I}-\text{I}$

**884.** The vapor density ( $\text{H} = 1$ ) up to  $700^\circ \text{C}$ . is 126.5, showing that the molecule is  $\text{I}_2$ . But at  $1400^\circ \text{C}$ . it is about two-thirds as much, and on increasing the temperature a point is reached at which the density is about one-half, 63.3, and a farther increase of temperature no longer decreases the density—a very significant fact, showing that the molecule dissociates into atoms, and that the original molecule contains two atoms, and not more than two. The sp. gr. of solid iodine (water = 1) at  $17^\circ \text{C}$ . is 4.948 (GAY-LUSSAC). It melts at  $114.15^\circ \text{C}$ ., and boils at  $184.35^\circ \text{C}$ . (RAMSAY and YOUNG, 1886, *Jour. Chem. Soc.*, 49, 453).

**Occurrence.**—It is found in sea-water, in some salt springs, and in some vegetable growths. The quantity of iodine in sea-water is very small, but certain sea-weeds have the power of storing it up.

**885. Preparation.**—(1) Sea-weed is carbonized by heat in a retort. The residue, called *kelp*, is lixiviated with water, which dissolves the sodium iodide. It now contains carbonates, sulphates, sulphides, etc., from which it is partially freed by crystallizing. It is then mixed with one-eighth its bulk of  $\text{H}_2\text{SO}_4$ , and allowed to stand for 24 hours. The  $\text{CO}_2$  and  $\text{H}_2\text{S}$  pass off, and much of the newly formed  $\text{Na}_2\text{SO}_4$  crystallizes out. Finally  $\text{MnO}_2$  is added, heat applied, and iodine sublimes (*a*). After all the iodine has sublimed the bromine begins to be set free, and is condensed. The amount of bromine thus secured is about one-tenth that of the iodine. (2) Another method sometimes used is to precipitate the iodine by  $\text{CuSO}_4$  and  $\text{FeSO}_4$  (*b*), and then distill the  $\text{Cu}_2\text{I}_2$  with  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$ . (3) When the solution contains only traces of iodine, it is freed by nitro-hydrochloric acid, and filtered through lamp-black, which absorbs it.  $\text{KOH}$  solution is then added, which dissolves it (*c*). The residue after evaporation is then sublimed with  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$ .



**886. IODINE** is solid; in soft scales or hexagonal prisms, with a dark iron-gray color and graphitoidal lustre. It is precipitated as a brownish-black powder. It vaporizes very slightly at ordinary temperatures—with a characteristic odor, resembling chlorine, but more offensive. It melts at  $114.15^\circ \text{C}$ ., and boils at  $184.35^\circ \text{C}$ .; the vapor having an intense, bright violet color.

**887.** It is slightly soluble in water, dissolving in 7,000 parts; freely soluble in alcohol, ether, chloroform, carbon disulphide, petroleum naphtha, glyeerine, and in solutions of iodides (including  $\text{HI}$ ). All solutions of uncombined iodine have red-brown, brownish-yellow, or violet tints. *The carbon disulphide solution is violet* (marked distinction from bromine), the other solutions brownish-yellow (but little darker than those of bromine). Solutions by chemical combination are referred to in 889.

**888. Starch-paste** is colored blue by a little iodine, violet by a further addition of iodine; and by still greater excess a blue-green (or, in presence of bromine, a brown) color is produced. This test is exceedingly delicate for iodine.\*

The iodized starch is decolorized by heating in solution to  $70^\circ$  or  $80^\circ \text{C}$ .

\* *The union of iodine and starch* is probably an example of molecular adhesion rather than of union within molecules. When dry starch is saturated with ether solution of iodine, and exposed for some time to the heat of the water-bath, about 4 per cent. of iodine is retained. This corresponds nearly with the formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_{20}\text{I}$ . Prepared under other conditions, it holds 7 to 8 per cent. of iodine  $(\text{C}_6\text{H}_{10}\text{O}_5)_{10}\text{I}$ .

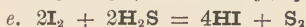
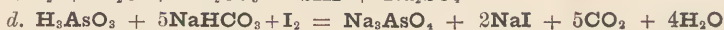
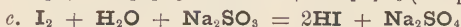
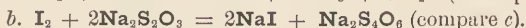
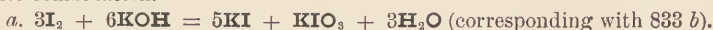
(158° to 176° F.), but regains its color on cooling. Its color is destroyed by strong chlorine, and by alkalies.

No compound of iodine colors starch.

**889.** Though expelled from combination with bases by chlorine, bromine, nascent oxygen, and other strong electro-negatives, iodine acts in many relations as an *oxidizing agent*, readily entering into combination, as iodides, when acted on by reducing agents. On the other hand, in relation to a limited number of active electro-negatives, it may act as a *reducing agent*, becoming the subject of oxidation, in the formation of iodates. Iodine chlorides also are formed,  $\text{ICl}_2$ ,  $\text{ICl}_3$ , and  $\text{ICl}_4$ , of yellow to brown colors.

Iodine slowly bleaches litmus and other vegetable colors, and stains the skin yellow-brown.

**Colorless solutions** are formed by all the alkali hydroxides with iodine; the fixed alkali hydroxides forming iodides and iodates (*a*). With **ammonia** in water solution, it dissolves more slowly, becoming colorless; the solution contains the most of the iodine as ammonium iodide, and liable to deposit a dark-brown powder, termed "*iodide of nitrogen*," very easily and violently *explosive* when dry. This substance is a variable substitution of one, two, or three atoms of **I** for **H** in  $\text{NH}_3$  (45 *c*). Among **reducing agents**, solutions of **thiosulphates** quickly dissolve and decolor iodine, forming iodides and a more highly oxidized acid of sulphur, tetrathionic acid (*b*). Solutions of **sulphites** and of **sulphurous acid** convert iodine into colorless hydriodic acid (*c*).—**Arsenious acid** in alkaline mixture is oxidized to an arsenate, and a colorless iodide is formed (*d*). Hydrosulphuric acid dissolves iodine as hydriodic acid, the solution of which is so prepared (*e*). *The alkali hydroxides, and reducing agents, decolor iodized starch*, by taking its free iodine into combination.



The chief **Acids of Iodine** are :

Hydriodic acid,  $\text{HI}^{\text{I}}$ .

Iodic acid,  $\text{HI}^{\text{V}}\text{O}_3$ .

Periodic acid,  $\text{HI}^{\text{VII}}\text{O}_4$ .

**890. Estimation.**—The estimation of free iodine is important, for upon it depends the determination of a large class of substances which liberate iodine from **KI** (*e.g.*, chlorine, bromine, etc.), or which, when boiled with **HCl**, yield **Cl** (*e.g.*, the higher oxides and metallic acids). The usual method is to add a standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$ , in presence of a little starch-paste, to show when the action is complete.



**891. Oxidation.**—When iodine oxidizes it becomes  $\text{I}^{\text{I}}$ ; that is, either hydriodic acid or an iodide. When it reduces it becomes  $\text{I}^{\text{V}}$  or  $\text{I}^{\text{VII}}$ ; that is, iodic acid or an iodate or a periodate. *b*. For its action on  $\text{HNO}_3$ , see 733;  $\text{H}_4\text{Fe}(\text{CN})_6$ , 691;  $\text{H}_3\text{PO}_4$ , 756;  $\text{H}_2\text{S}$ , 785;  $\text{H}_2\text{SO}_3$ , 813; **Cl**, 834;  $\text{HClO}_3$ , 863; **Br**, 868.



Hg'	c.	Becomes Hg'' in presence of alkalies and acids.		
Sn''	d.	Becomes Sn <sup>IV</sup>	"	"
Sb'''	e.	Becomes Sb <sup>V</sup> in presence of alkalies only.		
As'''	f.	Becomes As <sup>V</sup>	"	"
Mn <sup>IV</sup>	g.	Becomes Mn <sup>IV</sup>	"	"
Co''	h.	Becomes Co'''	"	"
Fe''	i.	Becomes Fe'''	"	"
Cr'''	j.	Becomes Cr <sup>VI</sup>	"	"
Ni''	k.	Is not changed by iodine.		

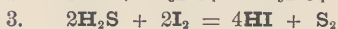
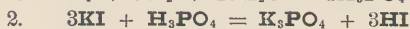
## HYDRIODIC ACID. HI.

Oxidation valence.....H/I'

Structural valence.....H-I

**892.** Vapor density ( $H=1$ ) is 63.7. At  $0^{\circ} C$ . a pressure of four atmospheres liquefies it. Under ordinary atmospheric pressure it solidifies at  $-51^{\circ} C$ . (FARADAY).

**Preparation.**—(1) By action of **P** on iodine and separation by distillation. (2) By adding  $H_3PO_4$  to **KI** and distilling. (3) By action of  $H_2S$  on iodine and distilling.

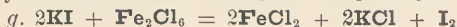
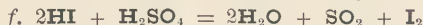
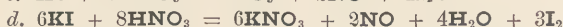
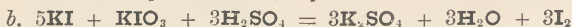


**893.** Absolute hydriodic acid is **gaseous** at ordinary temperatures, but freely soluble in water; being easily obtained in **solution** containing 50 to 60 per cent. of acid, and having a boiling point above that of water, but giving off some vapor at common temperatures. Both the gas and the solution are colorless, and redden litmus. Hydriodic acid *decomposes* gradually in the air with separation of iodine—more rapidly at higher temperatures; so that the evolved gas is always strongly colored with iodine, and the exposed solution commences at once to turn brownish-yellow with the free iodine dissolved by the acid. The liberated gas has a slight chlorine-like odor, and a stronger *offensive odor* (due to both the iodine and hydriodic acid). Upon brief exposure, both the gas and the solution give abundantly the reactions of free iodine (with starch, carbon disulphide, etc.)

**894.** Like hydrochloric and hydrobromic acids, *hydriodic acid is produced by transposition from the metallic iodides*, by the action of **dilute sulphuric acid**; but an attempt to separate the **HI** by distillation would result in its decomposition, as shown in equation *f*. Also, by large excess of **hydrochloric** and **hydrobromic** acids. The iodides of silver, lead, mercury, and tin are transposed with difficulty by sulphuric acid, more readily by hydrochloric acid.

895. The iodides (including hydrogen iodide) are decomposed by oxidizing agents more readily than the bromides.

Ozone promptly decomposes all iodides, not excepting those of the alkali metals ; while atmospheric oxygen decomposes hydriodic acid and iron and calcium iodides but slowly, and alkali iodides not at all. *Iodine* is liberated from iodid at once by **chlorine**, **bromine** (*a*), **iodic acid** (*b*), and bromic acid. Iodine is first set free and then oxidized to *iodic acid*, by **acidulated chlorate**, by **hypochlorites** (with occurrence of iodine chlorides and final formation of periodates), and by concentrated **nitric acid** with heat (*c*); dilute nitric acid slowly separating iodine (*d*), and scarcely decomposing lead, silver, and mercury iodides. Acidulated **potassium nitrite** acts more promptly than nitric acid. **Manganese dioxide** with sulphuric acid is employed in the manufacture of iodine (*e*). **Permanganate** solution, added in excess, produces *iodates*, iodine being first separated and at last all oxidized ; in neutral or alkaline dilute solutions (1 part salt to 240 parts water), a distinction from bromides, which do not decolor the permanganate. **Chromates**, acidulated, cause immediate separation of iodine. **Concentrated sulphuric acid** (*f*) and **ferric chloride** (*g*) are reduced by iodides. Further, see 907.



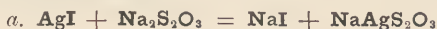
896. The metallic iodides are all **soluble in water**; *except* those of **Ag**, **Pb**, and **Hg**, except palladous iodide, cuprous iodide, bismuth iodide decomposed by water, and stannous iodide sparingly soluble in water. Lead iodide is sparingly soluble, and mercuric iodide very sparingly soluble, in water.

The *double iodides* of lead, silver, and mercury with alkali metals—as **KI.AgI** and **(KI)<sub>2</sub>HgI<sub>2</sub>**—are soluble in water; *i.e.*, the *iodides of first-group metals* are soluble in solutions of alkali iodides, by combination ; mercurous iodide in part only, as explained in 438.

Alcohol dissolves many of the iodides soluble in water—including the alkali iodides, and those of barium and calcium—and dissolves mercuric, but not mercurous or argentic, iodide.

*Silver iodide* is but very sparingly soluble in concentrated solution of ammonium hydroxide, and insoluble in hot solution of ammonium acid carbonate (distinctions from the chloride). It dissolves in solution of potassium cyanide.

The iodides of silver and of lead are soluble by decomposition in solution of alkali thiosulphates (*a*); lead iodide in fixed alkalies (387). The iodides of silver and mercury are not decomposed, the iodide of lead slowly decomposed, by dilute nitric acid.



In **analysis**, iodides are most easily identified by the color of the carbon disulphide solution of liberated iodine (902). The silver precipitate of iodide is separable from chloride by solution of the latter in ammonium hydroxide (921).

**897. Silver nitrate** solution in excess precipitates, from solutions of iodides, *silver iodide*,  $\text{AgI}$ , yellow-white, blackening in the light (without notable separation of iodine). For the solubilities of the precipitate, see 896, and compare 414. For its separation from chloride and bromide, see further 921.

Solution of mercuric chloride precipitates the bright, yellowish-red to red, *mercuric iodide*,  $\text{HgI}_2$ . The precipitate redissolves on stirring, after slight additions of the mercuric salt, until equivalent proportions are reached, when its color deepens. For the solubilities of the precipitate see 446.—Solution of mercurous nitrate precipitates mercurous iodide,  $\text{Hg}_2\text{I}_2$ , further to green (see 438).

**898. Solution of plumbic nitrate** or acetate precipitates, from solutions of iodides not very dilute, *lead iodide*,  $\text{PbI}_2$ , bright-yellow—soluble, as stated in full in 392.

**899. Palladous chloride**,  $\text{PdCl}_2$ , precipitates, from solutions of iodides, *palladous iodide*,  $\text{PdI}_2$ , black, insoluble in water, alcohol, or dilute acids, and visible in 500,000 parts of solution. The reagent *does not precipitate bromine* at all in moderately dilute solutions, slightly acidulated with  $\text{HCl}$ . Palladous iodide is slightly soluble in excess of the alkali iodides, and is soluble in ammonium hydroxide (595).

**900. Copper sulphate**, with sulphurous acid or other reducing agent, precipitates from solutions of iodides the *cuprous iodide*,  $\text{Cu}_2\text{I}_2$ , which is *white*, if there is sufficient reducing agent to prevent the precipitation of iodine, brown. The precipitate is not altogether insoluble in water; therefore the filtrate responds to the delicate tests for iodine (*equation in 345 b*). *Bromine is not precipitated* with copper.

**901. Concentrated sulphuric acid** decomposes iodides, solid or in concentrated solution, with the reaction stated at 895 *f*. The evolved *gas* has the violet color of iodine, and the offensive odor of mingled iodine and hydriodic and sulphurous acids. When cooled and somewhat diluted, the *liquid* gives the iodine color with **starch** (888); or, on agitating gently with carbon disulphide, and permitting the latter to subside, the beautiful *violet tint* of iodine in this solvent.

**902. Chlorine-water** separates iodine more satisfactorily, in this test with carbon disulphide, especially from dilute solutions. The chlorine-water should be dilute and added (after the starch-paste or carbon disulphide) drop by drop; as an excess will destroy all characteristics of free iodine by formation of iodine chlorides and iodic acid (920).

**Nitrous acid**—as from zinc and nitric acid or from acidulation of ni-

trites—is a good agent to displace iodine. It should be very sparingly used (709). **Bromine** water is also employed for the same purpose.

Bromides do not interfere with the easy recognition of free iodine; unless an excess of chlorine is added no bromine will be liberated, and, if liberated, it does not modify the color of iodine, in starch or in carbon disulphide, unless the bromine is in much greater quantity, and even then the color represents iodine.

**903.** Solution of ferric chloride, added in the proportion of 6 or 8 drops to 3 or 4 cub. cent. (a fluid drachm or a little less) of the solution tested, together with carbon disulphide, slowly develops the violet tint in the subsiding liquid, if iodine is present (895 *g*)—a distinction from bromine.

For **Separation** of iodides from chlorides and bromides, 920; from iodates, 913.

**904.** The iodides of the alkali metals and of the first-group metals fuse without decomposition; those of mercury sublime undecomposed; but other non-alkali iodides are mostly decomposed by ignition.

Treated in the cupric bead of microcosmic salt, as directed for chlorine in 848, iodides give an emerald *green* glass.

**905. Estimation.**—(1) Gravimetrically. It is precipitated by  $\text{AgNO}_3$ , and after gentle ignition weighed as  $\text{AgI}$ . (2) Volumetrically, by standard solution of  $\text{AgNO}_3$ , using a little  $\text{K}_2\text{Cr}_2\text{O}_7$  to show the completion of the reaction. (3) It is oxidized to free iodine by chlorine or other convenient oxidizing agent, and then determined by standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$ .

**906. Preparation of Iodides.**—(1) By direct union of the elements, but in some cases heat must be employed, and the metal must be in a fine state of division. (2) By action of  $\text{HI}$  on the hydroxides, oxides, and carbonates of the metals. (3) Iodides of the first group are best made by precipitation. (4) Many metals, especially when finely divided, dissolve in  $\text{HI}$  with evolution of hydrogen.

**907. Oxidation.**—*a.* For the action of  $\text{HI}$  on  $\text{H}_6\text{Fe}_2(\text{CN})_{12}$  see 694;  $\text{HNO}_2$ , 713;  $\text{HNO}_3$ , 733;  $\text{H}_2\text{SO}_4$ , 829;  $\text{Cl}$ , 834;  $\text{HClO}_3$ , 863;  $\text{Br}$ , 868;  $\text{HBrO}_3$ , 883.

$\text{HIO}_3$  *b.* Free iodine is liberated from both acids.

$\text{Pb}'' + n$  *c.* Becomes  $\text{Pb}''$  and  $\text{I}^\circ$  (free iodine).

$\text{As}^\vee$  *d.* Becomes  $\text{As}'''$  “  $\text{I}^\circ$ .

$\text{Sb}^\vee$  *e.* Becomes  $\text{Sb}'''$  “  $\text{I}^\circ$ .

$\text{Cu}''$  *f.* Becomes  $\text{Cu}'$  “  $\text{I}^\circ$ .

$\text{Co}'''$  *g.* Becomes  $\text{Co}'$  “  $\text{I}^\circ$ .

$\text{Ni}'''$  *h.* Becomes  $\text{Ni}''$  “  $\text{I}^\circ$ .

$\text{Fe}'''$  *i.* Becomes  $\text{Fe}''$  “  $\text{I}^\circ$ .

$\text{Cr}^{\text{VI}}$  *j.* Becomes  $\text{Cr}'''$  “  $\text{I}^\circ$ .



**Mn'' + n k.** Becomes **Mn''**, and if **HI** is in excess **I°** is formed. If dilute hydriodic acid with **K<sub>2</sub>Mn<sub>2</sub>O<sub>8</sub>** is used manganese peroxide is first formed, and if the permanganate is in great excess potassium iodate is formed.

### IODIC ACID, **HIO<sub>3</sub>**.

Oxidation valence..... **H'IvO<sup>-''</sup><sub>3</sub>**  
 $\text{O}$

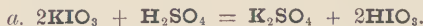
Structural valence..... **H-O- $\overset{\text{O}}{\underset{\text{O}}{\text{I}}}=\text{O}$**

**908. Preparation.**—(1) By boiling **I** with **HNO<sub>3</sub>**, sp. gr. 1.42, or, better, the fuming, sp. gr. 1.48. (2) By treating **I** with **Cl** or **HClO** in presence of **H<sub>2</sub>O**. (3) By transposing iodates with stronger acids, as **Ba(IO<sub>3</sub>)<sub>2</sub>** with **H<sub>2</sub>SO<sub>4</sub>**, using the latter slightly in excess, and after filtering from the insoluble **BaSO<sub>4</sub>** the **HIO<sub>3</sub>** is separated from the remaining **H<sub>2</sub>SO<sub>4</sub>** by crystallization. (4) Formed by action of auric oxide on **I**. (5) By action of **AgNO<sub>3</sub>** on **I**.

1.  $3\text{I}_2 + 10\text{HNO}_3 = 6\text{HIO}_3 + 10\text{NO} + 2\text{H}_2\text{O}$
2.  $\text{I}_2 + 5\text{Cl}_2 + 6\text{H}_2\text{O} = 2\text{HIO}_3 + 10\text{HCl}$
4.  $3\text{I}_2 + 5\text{Au}_2\text{O}_3 + 3\text{H}_2\text{O} = 6\text{HIO}_3 + 10\text{Au}$
5.  $5\text{AgNO}_3 + 3\text{I}_2 + 3\text{H}_2\text{O} = 5\text{AgI} + 5\text{HNO}_3 + \text{HIO}_3$

**909. Absolute iodic acid, HIO<sub>3</sub>** (or **H<sub>2</sub>I<sub>2</sub>O<sub>6</sub>**), is a white, crystallizable, odorless solid, *permanent* in the air; at 170° C. (338° F.) resolved into water and iodic anhydride (**H<sub>2</sub>O** and **I<sub>2</sub>O<sub>5</sub>**). Iodic anhydride is a crystallizable solid, at 300° C. resolved into iodine and oxygen. Bromic anhydride is not known. Iodic acid is freely soluble in water and in alcohol; the solutions reddening litmus, and afterwards bleaching it.\*

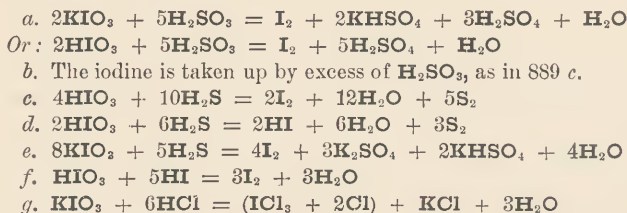
**910.** Iodic acid is formed by prolonged action of nitric acid and other oxidizing agents upon iodine. Its salts, the iodates, are formed together with iodides in dissolving iodine in aqueous alkalis (889 *a*), as well as by oxidation of iodides (895). Iodic acid is easily obtained by transposing metallic iodates with sulphuric acid (*a*); its radical not easily breaking up when separated from metals, as chloric and bromic acids do.



**911. The Iodates**—including hydrogen iodate—are decomposed by **reducing agents**, with the formation of iodides (of metals or of hydrogen) and with other results.

**Sulphurous acid** is oxidized by iodic acid, first with separation of *iodine* (*a*); then, by excess of the sulphurous acid, with formation of *hydriodic acid* (*b*). Hence, sulphurous acid, added *short of saturation*, with **starch**, forms a delicate test for iodates, and a distinction from iodides; but excess of the reagent destroys the color. **Thiosulphates** produce iodine, or hydriodic acid. **Hydrosulphuric acid** also reduces iodates, precipitating at first iodine and sulphur (*c*). With excess of the reducing agent, the final products are hydriodic acid and sulphur (*d*); with excess of the iodate, iodine and sulphate (*e*). **Hydriodic acid** instantly separates, from iodic acid, all the iodine of both acids (*f*); hence, an intermixture of a metallic iodate with an iodide is revealed at once by adding a dilute or weak acid that will not itself liberate iodine, but will produce both the acids of iodine, so that they can decompose each other. In solution of potassium iodide, for example, a slight addition of **tartaric acid** shows the presence of iodate by the *immediate*, not progressive, appearance of the iodine color, the test being more delicate by use of carbon disulphide. In solutions not of iodides, an **iodide** may be added,

with tartaric or **acetic acid**, in search for iodates. But it must be remembered that pure iodides, so treated, form hydriodic acid, which, by atmospheric oxidation, *progressively* liberates iodine, and will soon give a deep color to starch or carbon disulphide. **Hydrochloric acid** forms with iodates mostly iodine chlorides (*g*), iodine not being liberated (distinction from bromates, 882). **Morphia** reduces iodic acid, with separation of iodine as a final product. Further, see 916.



Iodates *in dry mixture* with combustible bodies are reduced, on heating or concussion, with *detonation*, but much less violently than chlorates or nitrates. Heated alone, iodates are either reduced to iodides with liberation of oxygen (iodates of potassium, sodium); or to oxides with liberation of iodine and oxygen (iodate of barium). Compare Bromates, 879.

**912.** The iodates are either **insoluble or sparingly soluble in water**, except those of the alkali bases, a marked difference from bromates and chlorates. Barium, silver, and lead iodates are insoluble in water. The alkali metals form acid iodates. In alcohol most of the iodates are insoluble; barium iodate, insoluble; calcium and potassium iodates, scarcely at all soluble (distinctions from iodides).

*Silver iodate* is readily soluble in **ammonium hydroxide** (distinction from iodide); it is slightly soluble in dilute nitric acid (more so than the iodide).

Iodates are **identified** by separation of free iodine, known by its color in carbon disulphide solution or in mixture with starch (911); and by precipitation of barium salt (912).

**913.** Solution of **silver nitrate** precipitates, from even very dilute solutions of iodates and from solutions of iodic acid if not very dilute, *silver iodate*,  $\text{AgIO}_3$ , white, crystalline, soluble in ammonium hydroxide, soluble in an excess of hot  $\text{HNO}_3$ . *In the ammonia solution, hydrosulphuric acid* precipitates *silver iodide*.

**Barium chloride** precipitates *barium iodate*,  $\text{Ba}(\text{IO}_3)_2$ , nearly insoluble in cold and little soluble in hot water, insoluble in alcohol, scarcely soluble in dilute nitric acid, readily soluble in dilute hydrochloric acid. Hence, dilute solutions of free iodic acid should either be neutralized or tested with barium nitrate. This precipitate, by addition of alcohol, is a complete *separation from iodides*, and, when well washed, decomposes with a very little sulphurous acid (911 *a*), and found to color carbon disulphide violet, its evidence for iodic acid is conclusive. Barium iodate is transposed with ammonium carbonate, on digestion in solution and with ammonium hydroxide (separation from periodate).

Salts of **lead** give a white precipitate of *lead iodate*,  $\text{Pb}(\text{IO}_3)_2$ . Ferric chloride gives, in solutions not dilute, a yellowish-white precipitate of *ferric iodate*,  $\text{Fe}_2(\text{IO}_3)_6$ , sparingly soluble in water, and freely soluble in *excess of the reagent*. Boiling decomposes it.

**Alcohol** precipitates *potassium iodate* from water solution, an approximate separation from iodide.

**914.** Iodates of the alkalis and alkaline earths are easily made by the action of iodine on the hydroxides, and separation by alcohol or by crystallization from the iodides which are formed in the reaction. All iodates may be made by action of the acid on the

hydroxides or carbonates. A few are best made by precipitation. The precise composition of many of the iodates has not been determined.

**915. Estimation.**—(1) By precipitation with  $\text{AgNO}_3$ , and, after drying at  $100^\circ \text{C}$ ., weighing as  $\text{AgIO}_3$ . (2) By reducing to  $\text{HI}$  or an iodide and then proceeding as directed in 905. (3) Volumetrically, by treating with  $\text{HI}$  and estimating the free iodine liberated.

**916. Oxidation.**—*a.* For action on  $\text{H}_2\text{C}_2\text{O}_4$  see 659;  $\text{H}_6\text{Fe}_2(\text{CN})_{12}$ , 694;  $\text{HCNS}$ , 702;  $\text{HNO}_2$ , 713;  $\text{H}_3\text{PO}_2$ , 756;  $\text{H}_2\text{S}$ , 785;  $\text{H}_2\text{SO}_3$ , 813;  $\text{Cl}$ , 834;  $\text{HBr}$ , 876;  $\text{HI}$ , 907.

$\text{Sn}''$  *b.* Becomes  $\text{Sn}^{\text{IV}}$  and  $\text{I}^-$ .

$\text{Sb}'''$  *c.* Becomes  $\text{Sb}^{\text{V}}$  and  $\text{I}^\circ$ .

$\text{As}'''$  *d.* Becomes  $\text{As}^{\text{V}}$  and  $\text{I}^\circ$ .

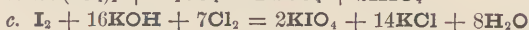
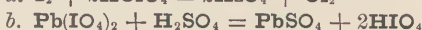
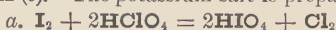
$\text{Fe}''$  *e.* Becomes  $\text{Fe}'''$  and  $\text{I}^\circ$ .

### PERIODIC ACID. $\text{HIO}_4$ or $\text{H}_5\text{IO}_6$ .

Oxidation valence..... $\text{H}'\text{I}^{\text{VII}}\text{O}^{--}$ , or  $\text{H}'\text{I}^{\text{VII}}\text{O}^{--}$ .

Structural valence..... $\text{H}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{I}}}=\text{O}$ , or  $\text{H}-\text{O}-\overset{\text{H}}{\underset{\text{O}}{\text{I}}}(\text{O}-\text{H})_2$

**917. Preparation.**—(1) By action of  $\text{HClO}_4$  on  $\text{I}$  (*a*). (2) By action of  $\text{H}_2\text{SO}_4$  on  $\text{Pb}(\text{IO}_3)_2$  (*b*). (3) Periodate of sodium is made by action of  $\text{Cl}$  upon  $\text{I}$ ,  $\text{NaI}$ , or  $\text{NaIO}_3$  in solution of  $\text{NaOH}$  (*c*). The potassium salt is prepared in a similar manner.



Neither the anhydride nor the acid  $\text{HIO}_4$  has been isolated. Only  $\text{HIO}_4$ , with two molecules of water, has been crystallized. One view represents the normal acid as  $\text{HIO}_4$ , which is supported by the actual preparation of the corresponding salts, such as  $\text{KIO}_4$ ,  $\text{AgIO}_4$ ,  $\text{Pb}(\text{IO}_4)_2$ , etc. Another view represents the normal acid as  $\text{H}_5\text{IO}_6$  ( $\text{HIO}_4 \cdot 2\text{H}_2\text{O} = \text{H}_5\text{IO}_6$ ). This view is supported by the actual production of  $\text{Ag}_5\text{IO}_6$ ,  $\text{Na}_5\text{IO}_6$ ,  $\text{Ba}_5(\text{IO}_6)_2$ , etc. The aqueous solution may be boiled, but at  $140^\circ \text{C}$ . it begins to decompose, forming first  $\text{HIO}_3$ , oxygen, and water; then  $\text{I}_2\text{O}_5$ , and finally free iodine and oxygen. Ignition reduces alkali periodates to iodides, evolving oxygen. Ignition also reduces other periodates in the same manner that it does iodates. They are all reduced by  $\text{HCl}$ , evolving  $\text{Cl}$ ; by  $\text{H}_2\text{SO}_3$ , giving first free iodine and then  $\text{HI}$ , and forming  $\text{H}_2\text{SO}_4$ ; and  $\text{HI}$  liberates free iodine, but only one-fourth of the total quantity in the salt (RAMMELSBURG). According to Lautsch, its behavior with  $\text{Hg}_2(\text{NO}_3)_2$  is characteristic. The pentasodic periodate,  $\text{Na}_5\text{IO}_6$ , gives a light yellow precipitate consisting of decamercurous periodate,  $\text{Hg}_{10}\text{I}_2\text{O}_{12}$ .



918. Comparison of Certain Reactions of the Acids of Chlorine, Bromine, and Iodine,  
*Taken in Water Solution, as Potassium Salts, or other Soluble Compounds.*

	Chlorides.	Bromides.	Iodides.	Chlorates.	Iodates.	Hypochlorites.
$\text{AgNO}_3$ , in excess...	$\text{AgCl}$ , white (842).	$\text{AgBr}$ , white (872).	$\text{AgI}$ , yellow-white (897).	No pre. (859).	$\text{AgIO}_3$ , white (912).	No pre. (853).
$\text{AgNO}_3$ , with excess of the solution tested.	Pre. ? (409).	Pre. (414).	Sol. (414).	.....	Pre.	.....
$\text{NH}_4\text{OH}$ , to the $\text{Ag}$ pre.	Dissolved.	In part dissolved.	Not dissolved.	.....	Dissolved.	.....
$\text{HgCl}_2$ , in excess	.....	No pre.	$\text{Hg}_2\text{I}_2$ , yellow-red.	No pre.	$\text{Hg}(\text{IO}_3)_2$ .	No pre.
$\text{HgCl}_2$ , with excess of the solution tested.	.....	No pre.	No pre. (446).	.....	Pre.	.....
$\text{Hg}_2(\text{NO}_3)_2$ , in excess	$\text{Hg}_2\text{Cl}_2$ , white.	$\text{Hg}_2\text{Br}_2$ , white.	$\text{Hg}_2\text{I}_2$ (887).	No pre.	Pre.	No pre.
$\text{BaCl}_2$	.....	.....	.....	.....	$\text{Ba}(\text{IO}_3)_2$ (913).	.....
$\text{CuSO}_4$ , with $\text{H}_2\text{SO}_3$	.....	.....	$\text{Cu}_2\text{I}_2$ (900).	.....	(911 <i>a</i> )	.....
$\text{H}_2\text{SO}_4$ , dilute	$\text{HCl}$ (soluble gas).	$\text{HBr}$	$\text{HI}$ (894)	$\text{HClO}_3$ , $\text{ClO}_2$ , $\text{Cl}$	$\text{HIO}_3$ (910).	$\text{Cl}$ (bleaches).
$\text{HCl}$	.....	$\text{HBr}$	$\text{HI}$	$\text{ClO}_2$ and $\text{Cl}$	.....	$\text{Cl}$
$\text{Cl}$	.....	$\text{Br}$ (873).	$\text{I}$ (902).	.....	.....	.....
Chromate, with $\text{H}_2\text{SO}_4$	$\text{CrO}_2\text{Cl}_2$ (845).	$\text{Br}$	$\text{I}$	.....	.....	.....
$\text{K}_2\text{Mn}_2\text{O}_8$ , dilute, neutral	.....	.....	$\text{I}$ (895).	.....	.....	.....
$\text{Na}_2\text{SO}_3$ , with $\text{H}_2\text{SO}_4$	.....	.....	.....	Chlorides.	$\text{I}$ and $\text{HI}$ (911).	$\text{HCl}$
$\text{H}_2\text{S}$	.....	.....	.....	$\text{S}$ , $\text{H}_2\text{SO}_4$ (785).	$\text{I}$ , $\text{HI}$ , $\text{S}$ (911).	$\text{S}$ , $\text{H}_2\text{SO}_4$ .



**919. THE SEPARATION** of the acids of **chlorine**, **bromine**, and **iodine** is effected by oxidations, reductions, color solutions, precipitations, separative solutions, and vaporizations. In many cases of separation, the acids to be separated will act upon each other.

**920. The Recognition** of chlorides, bromides, and iodides—by evolving their chlorine, bromine, and iodine, *in presence of each other*—can be accomplished as follows—for the iodine the test being very easy; for chlorine, indirect but unmistakable; for bromine, dependent upon much care and discretion.\*

The **Iodine** is liberated with dilute **chlorine-water**, added drop by drop, and is readily detected by **starch**, or **carbon disulphide**, according to 902. (As to interference of thiocyanates, see 701.) The **Chlorine** is vaporized (from another portion) as *chlorochromic anhydride*, and the latter identified by its color and its various products, as described in 845. Before the **Bromine** is identified the iodine is to be either *removed as free iodine*, or *oxidized to iodate* (873). The oxidation to iodic acid is effected as follows: Treat with good chlorine-water till free iodine no longer shows its color; add a drop or two more of the chlorine-water, and dilute with water, keeping cool; then add the carbon disulphide, agitate, and leave the solvent to settle, for the yellow color of bromine. The removal of free iodine may be done as follows: Add chlorine-water, drop by drop, as long as the iodine tint seems to deepen by the addition; add the carbon disulphide, agitate, leave to subside, and remove the lower layer, either by taking it out with a pipette, or by filtration through a wet filter. Repeat, if need be, till iodine color is no longer obtained; then continue, with dilute chlorine-water, in test for bromine.

If iodine in large proportion is to be removed, it is well, first, to precipitate it out, as far as possible, by copper sulphate and a reducing agent, as directed in 922. The filtrate is then to be treated by either method above given.

**921. The Separation by ammonium hydroxide**, as a solvent of the silver precipitates—**AgCl**, **AgBr**, **AgI**—when conducted with dilute ammonium hydroxide, may be made nearly complete between the chloride and the iodide, but it is very imperfect between the bromide and either of the others. The hot and strong solution of ammonium acid carbonate separates the chloride from the bromide (compare 843, 872, 896).

**922. The direct removal of iodides by precipitation**, leaving bromides and chlorides in solution, can be effected (approximately) by **copper sulphate with sulphurous acid** (900), or quite completely by **palladous chloride** (899). With the copper sulphate, the reduction ought to be thorough; and this result is better secured by sulphurous acid than by ferrous sulphate, and without loading the solution with another metallic salt. The action of palladium chloride is subject to no objection, except the scarcity and expensiveness of the reagent.

**923. Chloric acid** is separated from *hydrochloric and all other acids of chlorine, bromine, and iodine* (except from hypochlorous acid, and from traces of bromic acid), by remaining in solution during the precipitation by **silver nitrate** (859).

**924. Chloric acid** is separated from *nitric acid*—after finding that *silver nitrate gives no precipitate* in another portion of the solution, acidulated—by evaporating and igniting the residue, then dissolving, and testing one portion of the solution by **silver nitrate** for the *chloride* formed from chlorate during ignition (858). The other portion of the solution is tested for nitric or nitrous acid.

\* In consequence of the relative commercial values of bromine and iodine, and the medicinal relations of bromides and iodides, it is of great importance to search commercial iodides for intentional and considerable mixtures of bromides—an impurity likely to escape cursory chemical examination. There are, however, very slight and usually unobjectionable proportions of bromides generally to be found in the iodides of commerce, and occurring from the difficulty of exact separation in the manufacture of iodine from kelp.

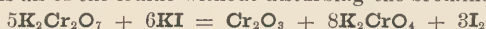
925. If we have to separate chloric acid *both from nitric and hydrochloric acids*, a solution of **silver sulphate** must be used instead of the nitrate, to precipitate out all the hydrochloric acid. The filtrate from this is evaporated, **ignited**, dissolved and tested, as in 924, for chloride, indicating chlorate in the original solution, and another portion is tested for nitric acid. Also, chlorates are *distinguished* (not separated) *from nitrates*, by oxidation of **ferrous sulphate** in solution with **acetic acid** on heating, and the consequent formation of the *red solution of ferric acetate* (218, 635). The solution tested must contain no free acids, and no nitrites or other oxidizing agents beside the two in question, but may contain chlorides; and, of course, the ferrous sulphate must be pure enough not to color when heated alone with the acetic acid. Mix the ferrous sulphate solution with the acetic acid, boil, then add the solution to be tested, and heat nearly to boiling, for some minutes. If no red color appears, chlorates are absent, and nitrates may be present.

926. **Hypochlorites** are separated *with chlorates* from chlorides (bromides), etc., by **silver nitrate**; and distinguished *from chlorates* (in the filtrate from **AgCl**, etc.) by bleaching litmus, and by their much more rapid decomposition and consequent precipitation of any silver in solution. They are also more active than chlorates, as oxidizing agents.

927. The identification of **iodic acid** is simple and certain, by use of **reducing agents** (911), or precipitants (913). The identification of **bromic acid**, in presence of other acids, is indicated in 880 to 882.

928. G. VORTMAN's method of detecting chlorine in presence of bromine and iodine is as follows: The solution containing the halogens combined with the alkali or alkali earth metals is heated with acetic acid and peroxide of lead until the supernatant liquid is colorless and has no longer the slightest odor of iodine or bromine; in this way the whole of the bromine and part of the iodine are driven off, the remainder of the latter remaining as iodate of lead along with the excess of lead peroxide. This is filtered off, the precipitate washed with boiling water, and the chlorine precipitated from the filtrate by addition of silver nitrate.

M. DECHAN's method (*Jour. Chem. Soc.*, 1886, 49, 682) consists (1) in boiling the mixture with a solution of 40 grammes of  $\text{K}_2\text{Cr}_2\text{O}_7$ , dissolved in 100 c.c. of water, which liberates and expels all of the iodine without disturbing the bromine and chlorine.



(2) 8 c.c. of a dilute solution of sulphuric acid (consisting of equal volumes of  $\text{H}_2\text{SO}_4$  sp. gr. 1.84, and water) are added to 100 c.c. of the dichromate solution, and on boiling the bromine is distilled off without disturbing the chlorine; after which the chlorine is detected in the usual manner.

For A. LONG's process for the analysis of a mixture of chlorides, bromides, iodides, chlorates, bromates, iodates, ferrocyanides, and ferricyanides, see *Chem. News*, 47, 209.

## EQUATIONS.

929. It is recommended that the student write all the equations representing the analysis, oxidation, and properties of all compounds, and *balance them according to the rule* given in 615. It will be seen that in most cases an oxidizing agent is made to act on two reducing agents, usually both in the same salt; or double reduction may occur—thus in No. 25  $\text{PbO}_2$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{KCl}$ , and  $\text{H}_2\text{O}$  are formed; in No. 66,  $\text{K}_2\text{MnO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{NO}$ , and  $\text{CO}_2$ ; in No. 57,  $\text{K}_2\text{CrO}_4$ ,  $\text{K}_2\text{MnO}_4$ ,  $\text{KCl}$ , and  $\text{CO}_2$ ; in No. 80, the **Mn** of both compounds is oxidized; in No. 17, **Hg**, **As**,  $\text{SnCl}_4$ , and  $\text{H}_2\text{O}$  are formed; in No. 21, **Pb**,  $\text{Na}_2\text{S}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ ; in Nos. 15 and 61 there is no action. In balancing equations for

recitation, the student should in all cases give his *authority for each equation*. It is to be understood that the second substances in each equation are to be used in *excess*, or in as great quantities as may be necessary to *fully oxidize or reduce* the substance placed first. Unless otherwise expressed,  $\text{H}_2\text{SO}_4$  means the dilute acid. It is advised that the teacher extend this list to several hundred for class use. The frequent introduction of blank equations like Nos. 15 and 61 has proven instructive.

1.  $\text{Mn}(\text{OH})_2 + \text{PbO}_2 + \text{HNO}_3$
2.  $\text{Pb}_3(\text{AsO}_4)_2 + \text{KOH} + \text{Cl}_2$
3.  $\text{Sn} + \text{HNO}_3$  (sp. gr. 1.40)
4.  $\text{Pb}_3(\text{AsO}_4)_2 + \text{Al} + \text{KOH}$
5.  $\text{Mn}(\text{H}_2\text{PO}_4)_2 + \text{KClO}_3 + \text{K}_2\text{CO}_3$  (fusion)
6.  $\text{K}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 + \text{C}$  (fusion)
7.  $\text{MnS} + \text{PbO}_2 + \text{H}_2\text{SO}_4$  (hot dilute)
8.  $\text{SnS} + \text{KOH} + \text{Cl}_2$
9.  $\text{Fe}(\text{OH})_2 + \text{H}_2\text{SO}_4$  (sp. gr. 1.83 hot)
10.  $\text{Pb}_3(\text{AsO}_4)_2 + \text{Zn} + \text{H}_2\text{SO}_4$
11.  $\text{Cr}_2(\text{SO}_4)_3 + \text{Mn}(\text{NO}_3)_2 + \text{K}_2\text{CO}_3$  (fusion)
12.  $\text{MnSO}_3 + \text{KOH} + \text{I}_2$
13.  $\text{Zn}_3\text{O}_5\text{CrO}_4 + \text{SnCl}_2 + \text{KOH}$
14.  $\text{NiC}_2\text{O}_4 + \text{KOH} + \text{Cl}_2$
15.  $\text{Fe} + \text{HNO}_3$  (sp. gr. 1.42 cold; see 929)
16.  $\text{KClO}_3$  (ignition)
17.  $\text{Hg}_3(\text{AsO}_4)_2 + \text{SnCl}_2 + \text{HCl}$  (sp. gr. 1.20)
18.  $\text{Na}_2\text{S}_4\text{O}_6 + \text{NaOH} + \text{Cl}_2$
19.  $\text{Al} + \text{KOH}$
20.  $\text{MnS} + \text{KNO}_3 + \text{K}_2\text{CO}_3$  (ignition)
21.  $\text{PbSO}_4 + \text{NaHCO}_3 + \text{C}$  (fusion)
22.  $\text{CrO}_3 + \text{H}_2\text{SO}_4$  (sp. gr. 1.83 hot)
23.  $\text{BiBr}_3 + \text{KOH} + \text{Cl}_2$
24.  $\text{Mn}_3\text{O}_4 + \text{Pb}_3\text{O}_4 + \text{HNO}_3$
25.  $\text{PbC}_2\text{O}_4 + \text{KOH} + \text{Cl}_2$
26.  $\text{Fe} + \text{H}_2\text{SO}_4$
27.  $\text{BiAsO}_4 + \text{Na}$  (amalgam)
28.  $\text{Cr}_2\text{Cl}_6 + \text{KClO}_3 + \text{K}_2\text{CO}_3$  (fusion)
29.  $\text{Mn}(\text{OH})_2 + \text{K}_2\text{Mn}_2\text{O}_8 + \text{H}_2\text{SO}_4$
30.  $\text{MnC}_2\text{O}_4 + \text{Pb}_3\text{O}_4 + \text{H}_2\text{SO}_4$  (hot dilute)
31.  $\text{FeS} + \text{KOH} + \text{Cl}_2$
32.  $\text{FeC}_2\text{O}_4 + \text{H}_2\text{SO}_4$  (sp. gr. 1.83 hot)
33.  $\text{K}_2\text{Cr}_2\text{O}_7$  (fusion)
34.  $\text{Mn}_3\text{O}_4 + \text{Mn}(\text{NO}_3)_2 + \text{K}_2\text{CO}_3$  (fusion)
35.  $\text{Mn}_3\text{O}_4 + \text{Cr}_2(\text{NO}_3)_6 + \text{K}_2\text{CO}_3$  (fusion)
36.  $\text{C} + \text{H}_2\text{SO}_4$  (sp. gr. 1.83 hot)
37.  $\text{Fe}_3(\text{AsO}_4)_2 + \text{KOH} + \text{Cl}_2$
38.  $\text{As}_4 + \text{HNO}_3$
39.  $\text{KClO}_4$  (ignition)
40.  $\text{Fe}_2\text{O}(\text{CrO}_4)_2 + \text{SnCl}_2 + \text{HCl}$
41.  $\text{FeBr}_2 + \text{KOH} + \text{Cl}_2$
42.  $\text{Cu}(\text{NO}_3)_2 + \text{Al} + \text{KOH}$
43.  $\text{MnS}_2\text{O}_3 + \text{KNO}_3 + \text{K}_2\text{CO}_3$  (ignition)
44.  $\text{Na}_2\text{S}_5\text{O}_6 + \text{NaHCO}_3 + \text{C}$  (fusion)
45.  $\text{FeBr}_2 + \text{HNO}_3$
46.  $\text{Cr}_2\text{I}_6 + \text{KOH} + \text{Br}_2$
47.  $\text{Mn}_2\text{O}_3 + \text{Pb}_3\text{O}_4 + \text{HNO}_3$
48.  $\text{Pb}(\text{H}_2\text{PO}_4)_2 + \text{KOH} + \text{Cl}_2$
49.  $\text{P}_4 + \text{KOH}$
50.  $\text{Hg}_3(\text{AsO}_4)_2 + \text{Na}$  (amalgam)
51.  $\text{Cr}_2(\text{SO}_4)_3 + \text{KClO}_3 + \text{K}_2\text{CO}_3$  (fusion)
52.  $\text{Bi}_6\text{O}_7(\text{CrO}_4)_2 + \text{SnCl}_2 + \text{KOH}$
53.  $\text{MnSO}_3 + \text{PbO}_2 + \text{H}_2\text{SO}_4$  (hot dilute)
54.  $\text{MnS}_2\text{O}_6 + \text{KOH} + \text{Cl}_2$
55.  $\text{K}_2\text{Mn}_2\text{O}_8 + \text{H}_2\text{SO}_4$  (sp. gr. 1.83 hot)
56.  $\text{AsH}_3$  (ignition in the air)
57.  $\text{Cr}_2\text{Cl}_6 + \text{Mn}(\text{ClO}_3)_2 + \text{K}_2\text{CO}_3$  (fusion)
58.  $\text{Cr}_2\text{O}_3 + \text{Cr}_2(\text{NO}_3)_6 + \text{K}_2\text{CO}_3$  (fusion)
59.  $\text{Bi}_2\text{O}(\text{CrO}_4)_2 + \text{SnCl}_2 + \text{KOH}$
60.  $\text{CoSO}_3 + \text{KOH} + \text{Cl}_2$
61.  $\text{Cu} + \text{HCl}$  (see 929)
62.  $\text{Fe}_2\text{O}_3$  (white heat)
63.  $\text{Ag}_3\text{AsO}_4 + \text{SnCl}_2 + \text{HCl}$  (sp. gr. 1.20)
64.  $\text{Na}_2\text{S}_5\text{O}_6 + \text{NaOH} + \text{Cl}_2$
65.  $\text{Pb}(\text{NO}_3)_2 + \text{Al} + \text{KOH}$
66.  $\text{MnS}_2\text{O}_6 + \text{KNO}_3 + \text{K}_2\text{CO}_3$  (ignition)
67.  $\text{Na}_2\text{S}_2\text{O}_3 + \text{NaHCO}_3 + \text{C}$  (fusion)
68.  $\text{PbMn}_2\text{O}_8 + \text{Zn} + \text{H}_2\text{SO}_4$
69.  $\text{FeI}_2 + \text{KOH} + \text{Br}_2$
70.  $\text{Mn}_3\text{O}_4 + \text{Pb}_3\text{O}_4 + \text{H}_2\text{SO}_4$
71.  $\text{HgC}_2\text{O}_4 + \text{KOH} + \text{Cl}_2$
72.  $\text{Fe} + \text{H}_2\text{SO}_4$  (sp. gr. 1.83 hot)
73.  $\text{SbCl}_3 + \text{Al} + \text{HCl}$
74.  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (ignition)
75.  $\text{Hg}_2\text{C}_2\text{O}_4 + \text{K}_2\text{Mn}_2\text{O}_8 + \text{H}_2\text{SO}_4$

- |   |  |
|---|--|
| 76. $\text{Mn}(\text{H}_2\text{PO}_4)_2 + \text{PbO}_2 + \text{H}_2\text{SO}_4$         | 84. $\text{PbO}_2 + \text{H}_2\text{SO}_4$ (sp. gr. 1.83 hot)                  |
| 77. $\text{FeSO}_3 + \text{KOH} + \text{Cl}_2$  | 85. $\text{Sb}_2\text{O}_3$ (ignitior)   |
| 78. $\text{Fe}(\text{H}_2\text{PO}_4)_2 + \text{H}_2\text{SO}_4$ (sp. gr. 1.83 hot)     | 86. $\text{Cu}_3\text{H}_2(\text{AsO}_4)_4 + \text{HI}$                        |
| 79. $\text{KNO}_3 + \text{NH}_4\text{Cl}$ (fusion)                                      | 87. $\text{SbI}_3 + \text{KOH} + \text{Cl}_2$                                  |
| 80. $\text{Mn}_2\text{O}_3 + \text{Mn}(\text{NO}_3)_2 + \text{K}_2\text{CO}_3$ (fusion) | 88. $\text{HgCrO}_4 + \text{Al} + \text{KOH}$                                  |
| 81. $\text{H}_3\text{AsO}_4 + \text{SnCl}_2 + \text{HCl}$ (sp. gr. 1.20)                | 89. $\text{Mn}_2\text{O}_4 + \text{KClO}_3 + \text{K}_2\text{CO}_3$ (ignition) |
| 82. $\text{S} + \text{H}_2\text{SO}_4$ (sp. gr. 1.83 hot)                               | 90. $\text{K}_2\text{Cr}_2\text{O}_7 + \text{NH}_4\text{Cl}$ (fusion)          |
| 83. $\text{Cr}_2\text{I}_6 + \text{KOH} + \text{Cl}_2$                                  | 91. $\text{KOH} + \text{I}_2$  |
|   | 92. $\text{Fe}_3(\text{AsO}_3)_2 + \text{KOH} + \text{I}_2$                    |

### PROBLEMS IN SYNTHESIS.

930. For the sake of more thorough drill in the principles of oxidation, a few problems are here given; a part of them the student should practically work at his table, but they are chiefly designed for class exercises. Special care should be taken that a pure product be formed, and that the ingredients be taken from the sources indicated. Thus, in the 31st, the chlorine for the ammonium chloride must be obtained from silver chloride, and the nitrogen of potassium nitrate must be converted into ammonia, and then united with the chlorine, and the product purified.

The student is not to suppose that these problems represent operations that are financially profitable, but merely chemical possibilities, and their solution will compel an accurate comprehension of a great variety of important principles. It is recommended that the teacher increase the number of these; an ordinary class may with profit discuss from three to five hundred. In each case the authority for each step in the process should be stated.

- |                                |                         |                        |
|--------------------------------|-------------------------|------------------------|
| 1. Make pure mercuric bromide, | from mercurous chloride | and aluminic bromide.  |
| 2. " chromic chloride,         | " potassium chromate    | " hydrochloric acid.   |
| 3. " arsenic acid,             | " potassium arsenite.   |                        |
| 4. " potassic arsenate,        | " potassium arsenite    | " potassium hydroxide. |
| 5. " plumbic nitrate,          | " plumbic chloride      | " zinc nitrate.        |
| 6. " mercurous nitrate,        | " mercuric chloride     | " bismuth nitrate.     |
| 7. " mercurous oxide,          | " mercuric oxide.       |                        |
| 8. " mercuric bromide,         | " metallic mercury      | " potassium bromide.   |
| 9. " mercuric bromide,         | " metallic mercury      | " silver bromide.      |
| 10. " lead nitrate,            | " lead dioxide          | " potassium nitrate.   |
| 11. " mercurous phosphate,     | " phosphoric acid       | " mercuric chloride.   |
| 12. " barium sulphate,         | " lead sulphide         | " barium hydroxide.    |
| 13. " bar'm hypophosphite,     | " calc'm hypophosphite  | " barium chloride.     |
| 14. " lead chromate,           | " chromic chloride      | " lead sulphate.       |
| 15. " chromic chloride,        | " potas. acid chromate  | " silver chloride.     |
| 16. " barium chromate,         | " chromic chloride      | " barium sulphate.     |
| 17. " mercuric chromate,       | " mercuric sulphide     | " chromium nitrate.    |
| 18. " chromium sulphate,       | " potas. acid chromate  | " bismuth sulphite.    |
| 19. " phosphoric acid,         | " sodium phosphate.     |                        |
| 20. " phosphorus,              | " calcium phosphate.    |                        |
| 21. " lead iodate,             | " lead sulphate         | " potassium iodide.    |
| 22. " silver iodate,           | " silver bromide        | " potassium iodide.    |
| 23. " ferric arsenate,         | " ferrous sulphide      | " arsenious acid.      |



24.	Make pure mercuric bromide,	from mercuric sulphide	and lead bromide.
25.	“ ammonium sulphate,	“ potassium nitrate	“ sulphur.
26.	“ ammonium chloride,	“ lead nitrate	“ silver chloride.
27.	“ sodium chloride,	“ sodium sulphate	“ silver chloride.
28.	“ phosphorus,	“ sodium phosphate.	
29.	“ lead sulphide,	“ triplumbic tetroxide	“ bismuth thiocyanate.
30.	“ ferrous sulphite,	“ ferrous chloride	“ barium sulphate.
31.	“ ammonium chloride,	“ potassium nitrate	“ silver chloride.
32.	“ mercurous nitrate,	“ mercuric chloride	“ potassium nitrate.
33.	“ potassium sulphate,	“ sodium sulphite	“ potassium nitrate.
34.	“ mercurous chloride,	“ mercurous sulphide	“ ferric chlorate.
35.	“ potassium iodide,	“ potassium chloride	“ sodium iodate.
36.	“ sodium iodate,	“ sodium chloride	“ potassium iodide.
37.	“ sodium phosphite,	“ potassium phosphate	“ sodium chloride.
38.	“ potassium bromide,	“ silver bromide	“ potassium chloride.
39.	“ potassium chloride,	“ silver chloride	“ potassium bromide.
40.	“ strontium nitrate,	“ strontium sulphate	“ mercurous nitrate.
41.	“ mercurous sulphide,	“ mercuric bromide	“ potassium sulphite.
42.	“ potassium sulphate,	“ sodium sulphate	“ potassium hydroxide.
43.	“ sodium sulphate,	“ potassium sulphate	“ sodium hydroxide.
44.	“ potassium chromate,	“ chromic chloride	“ potassium hydroxide.
45.	“ potassium iodide,	“ sodium iodate	“ potassium nitrate.
46.	“ sodium iodate,	“ potassium iodide	“ sodium nitrate.
47.	“ potassium chloride,	“ sodium chloride	“ potassium nitrate.
48.	“ potassium carbonate,	“ oxalic acid	“ potassium chloride.
49.	“ ammonium sulphate,	“ potassium nitrate	“ sodium sulphide.
50.	“ manganese peroxide,	“ lead permanganate.	
51.	“ arsenious sulphide,	“ lead arsenate	“ potassium thiocyanate
52.	“ arsenious sulphide,	“ lead arsenate	“ potassium sulphite.
53.	“ arsenious sulphide,	“ silver arsenate	“ barium sulphate.
54.	“ potassium nitrite,	“ sodium nitrite	“ potassium chloride.
55.	“ lead ferrocyanide,	“ cupric ferrocyanide	“ metallic lead.

## PART III.

### SYSTEMATIC EXAMINATIONS.

#### SEPARATION OF THE ACIDS FROM THE BASES.

931. The preliminary examination of the **Solid Material in the dry way** will give indications drawing attention to certain acids. Solutions can be evaporated to obtain a residue for this examination. Thus, *detonation* (not the decrepitation caused by water in crystals) indicates **chlorates**, **nitrates**, bromates, iodates. *Explosion or deflagration* will occur if these, or other oxygen-furnishing salts—as permanganates, chromates—are in mixture with easily combustible matter (858). Hypophosphites, heated alone, deflagrate intensely. A *brownish-yellow vapor* indicates **nitrates** or nitrites (730); a *green flame*, **borates** (636).—The *odor of burning sulphur* : **sulphides**, sulphites, thiosulphates, or free sulphur. The separation of *carbon black* : an organic acid. The formation of a *silver stain* : a **sulphur compound** (826).

932. When **dissolving a solid** by acids for work in the wet way, indications of the more volatile acids will be obtained. Sudden *effervescence* : a **carbonate** (oxalate or cyanate) (664, 665). *Greenish-yellow vapors* : a **chlorate** (860). *Brownish-yellow, chlor-nitrous vapors* on addition of hydrochloric acid : a **nitrate**.—The *characteristic odors* : salts of hydrosulphuric acid, sulphurous acid, hydrobromic acid, hydriodic acid, hydrocyanic acid, acetic acid.—The separation of *sulphur* : a higher **sulphide**, etc. It will be remembered that chlorine results from action of manganese dioxide, and numerous oxidizing agents, upon hydrochloric acid.

933. If the **Material is in Solution**, the bases will be first determined. (Certain volatile acids will be detected in the first-group acidulation—by indications mentioned in the preceding paragraph.) Now, it should first be considered, what acids *can be present in solution with the bases found*? Thus, if **barium** be among the bases; we need not look for sulphuric acid, nor, in a solution not acid, for phosphoric acid.

934. As a general rule, the non-alkali metals must be removed from a solution before testing it for acids, unless it can be clearly seen that they will not interfere with the tests to be made.

Metals need to be removed : because, firstly, *in the testing for acids by precipitation*, a precipitate may be obtained from the action of the reagent on the base of the solution tested, thus : if the solution contain silver, we cannot test it for sulphuric acid by use of barium chloride (and we are restricted to use of barium nitrate). And, secondly, *in testing for acids by transposition with a stronger acid*—the preliminary examination for acids—certain bases do not permit transposition. Thus, chlorides, etc., of lead, silver, mercury, tin, and antimony, and sulphide of arsenic, are not transposed by sulphuric acid, or not promptly.

935. If *neither arsenic nor antimony* is among the bases, they may all be removed (a) by *boiling with slight excess of sodium or potassium carbonate*, and filtering. *Arsenic and*

*antimony*, and all other bases of the second group, may be removed (*b*) by boiling with **hydrosulphuric acid**, and filtering. When the bases are removed by sodium or potassium carbonate, the filtrate *must be exactly neutralized* by nitric acid, with the *expulsion of all carbonic acid* by boiling. Then, for nitric acid, the original substance may be tested.

The filtrate, from the third or fourth group, though free from all bases which need to be removed, is not suitable material for general tests for acids; because it is loaded with ammonium salts, which act as solvents on many of the precipitates to be obtained.

**936.** The separation of **Phosphoric acid** from bases is a part of the work of the third group of metals, and is explained in 305 and 306. The removal of **Boracic acid**, **Oxalic acid**, **Silicic acid**, is described in 308.

The **non-volatile Cyanogen acids** can be separated from bases by digesting with potassium or sodium hydrate (not too strong, 684), adding potassium or sodium carbonate and digesting, and then filtering. The residue is examined for bases, by the usual systematic process. The solution (677 *c*) will contain the alkali salts of the cyanogen acids, and may contain metals whose hydroxides or carbonates are soluble in fixed alkali hydroxides.

## CONVERSION OF SOLIDS INTO LIQUIDS.

**937.** Before the fluid reagents can be applied, solids must be reduced to liquids. To obtain a complete solution, the following steps must be observed:

*First.* The solid, reduced to a fine powder, is boiled in ten times its quantity of **water**. Should a residue remain, it is allowed to subside, and the clear liquid poured off or separated by filtration. A *drop* or *two* evaporated on glass, or clean and bright platinum foil, will give a residue, if any portion has dissolved. If a solution is obtained, the residue, if any, is exhausted, and well washed with hot water.

*Second.* The residue, insoluble in water, is digested some time with hot **hydrochloric acid**. (Observe 932.) The solid, if any remain, is separated by filtration, and washed, first with a little of this acid, then with water. The solution, with the washings, is reserved.

*Third.* The well-washed residue is next digested with hot **nitric acid**. Observe if there are vapors of nitrogen oxides, indicating that a metal or other body is being oxidized (718). Observe if sulphur separates (564). If any residue remains it is separated by filtration and washing, first with a little acid, then with water, and the solution reserved.

Sometimes it does not matter which acid is used first. But if a first-group base be present **HNO<sub>3</sub>** should be added first, for **HCl** would form an insoluble chloride. If the substance contain tin (especially an alloy of tin) **HNO<sub>3</sub>** would form insoluble metastannic acid, **H<sub>10</sub>Sn<sub>5</sub>O<sub>15</sub>**, in which case **HCl** should be used first.

*Fourth.* Should a residue remain it is to be digested with **nitro-hydrochloric acid**, as directed for the other solvents.

The acid solutions are to be evaporated nearly to dryness, and then redissolved in water, acidulating, if necessary, to keep the substance in solution.

*Fifth.* Should the substance under examination prove insoluble in acids, it is likely to be either a sulphate (of barium, strontium, or lead); a chloride, or bromide, of silver or lead; a silicate or fluoride—perhaps decomposed by sulphuric acid—(745); and it *must be fused with a fixed alkali carbonate*, when the constituents are transposed in such manner as to render them soluble. The watery solution of the fused mass will be found to contain the acid; the residue, insoluble in water, the metal, now soluble in hydrochloric or nitric acids (compare 823).

If more than one solution is obtained, by the several trials with solvents, the material contains more than one compound, and the solutions, as separated by filtration, should be preserved separately, as above directed, and analyzed separately. *The separate results, in many cases, indicate the original combination of each metal.*

**CONVERSION OF SOLUTIONS INTO SOLIDS:** Before solids in solution can be subjected to preliminary examination—either for metals or for acids—they must be obtained in the solid state. This is done by evaporation.

## REMOVAL OF ORGANIC SUBSTANCES.

**938.** The methods of inorganic analysis do not provide against interference by organic compounds; and, in general, it is impossible to conduct inorganic analysis in material containing organic bodies. The removal of the latter can be effected, 1st, by combustion at a red or white heat, with or without oxidizing reagents; 2d (in part), by oxidation with potassium chlorate and hydrochloric acid on the water-bath; 3d, by oxidation with nitric acid in presence of sulphuric acid, at a final temperature of the boiling point of the latter; 4th, by solvents of certain classes of organic substances; 5th, by Dialysis. These operations are conducted as follows:

**939.** *Combustion at a red or white heat*, of course, excludes analysis for mercury, arsenious and antimonious bodies (except as provided in 520), and ammonium. The last-named constituent can be identified from a portion of the material in presence of the organic matter (45 and 705). If chlorides are present iron will be lost at temperatures much above 100° C., and potassium and sodium waste notably at a white heat, and slightly at a full red heat. Certain acids will be expelled, and oxidizing agents reduced.

The material is thoroughly dried and then heated in a porcelain or platinum crucible, at first gently. It will blacken, by separation of the carbon of the organic compounds. The ignition is continued until the black color of the carbon has disappeared. In special cases of analysis, it is only necessary to char the material; then pulverize it, digest with the suitable solvents, and filter; but this method does not give assurance of full separation of all substances. Complete combustion, without use of oxidizing agents, is the way most secure against loss, and entailing least change of the material; it is, however, sometimes very slow. The operation may be hastened, with oxidation of all materials, by *addition of nitric acid, or of ammonium nitrate*. The material is first fully charred; then allowed to cool till the finger can be held on the crucible; enough nitric acid to moisten the mass is dropped from a glass rod upon it, the lid put on, and the heat of the water-bath continued until the mass is dry, when it may be very gradually raised to full heat. This addition may be repeated as necessary. The ammonium nitrate may be added, as a solid, in the same way.

**940.** *Oxidation with potassium chlorate and hydrochloric acid on the water-bath* does not wholly remove organic matter, but so far disintegrates and changes it that the filtrate will give the group precipitates, pure enough for most tests. It does not vaporize any bases but ammonium, but of course oxidizes or chlorinates all constituents. It is especially applicable to viscid liquids; it may be followed by evaporation to dryness and ignition, according to 939.

The material with about an equal portion of hydrochloric acid is warmed on the water-bath, and a minute portion of potassium chlorate is added at short intervals, stirring with a glass rod. This is continued until the mixture is wholly decolorized and dissolved. It is then evaporated to remove chlorine, diluted and filtered. If potassium



and chlorine are to be tested for, another portion may be treated with nitric acid, on the water-bath. The organic matter left from the action of the chlorine or the nitric acid may be sufficient to prevent the precipitation of aluminium and chromium in the third group of bases; so that a portion must be ignited. As to arsenic and antimony, see 520.

941. The action of *sulphuric with nitric acid at a gradually increasing heat*, leaves behind all the metals (not ammonium), with some loss of mercury and arsenic (and iron?) if chlorides are present in considerable quantity. In this, as in the operations before-mentioned, volatile acids are lost—sulphides partly oxidized to sulphates, etc.

The substance is placed in a tubulated retort, with about four parts of concentrated sulphuric acid, and gently heated until dissolved or mixed. A funnel is now placed in the tubule, and nitric acid added in small portions, gradually raising the heat, for about half an hour—so as to expel the chlorine, and not vaporize chlorides. The material is now transferred to a platinum dish, and heated until the *sulphuric acid begins to vaporize*. Then add small portions of nitric acid, at intervals, until the liquid ceases to darken by digestion, after a portion of nitric acid is expelled. Finally, evaporate off the sulphuric acid, using the lowest possible heat at the close.

942. *The solvents used* are chiefly *ether for fatty matter*, and alcohol or ether, or both successively, for resins. Instead of either of these, benzene may be used; and many fats and some resins may be dissolved in petroleum naphtha. It will be observed, that ether dissolves some metallic chlorides, and that alcohol dissolves various metallic salts. Before the use of either of these solvents upon solid material, it should be thoroughly dried and pulverized. Fatty matter suspended in water solutions may be approximately removed by filtering through wet, close filters; also, by shaking with ether or benzene, and decanting the solvent after its separation.

943. *By Dialysis*, the larger part of any ordinary inorganic substance can be extracted in approximate purity from the greater number of organic substances in water solution. The degree of purity of the separated substance depends upon the kind of organic material. Thus, albuminoid compounds are almost fully rejected; but saccharine compounds pass through the membrane quite as freely as some metallic salts. (Consult *Watts' Dictionary*, II. 316; III. 715.)

## PRELIMINARY EXAMINATION OF SOLIDS.

944. Before proceeding to the analysis of a substance in the wet way, a careful study should usually be made of the reactions which the substance undergoes in the solid state, when subjected to a high heat, either alone or in the presence of certain reagents, before the blow-pipe, or in the flame of the Bunsen Burner. This examination in the dry way precedes that in the wet, and should be carried on systematically, following the plan laid down in the Tables, and noting carefully every change which the substance under investigation undergoes, and if necessary making reference to some of the standard works on Blow-pipe Analysis. In order to understand fully the nature of these reactions, the student should first acquaint himself with the character of the different parts of the flame, and the use of the blow-pipe in producing the reducing and oxidizing flames.

945. *The flame of the candle, or of the gas-jet*, burning under ordinary circumstances, consists of three distinct parts: a dark nucleus or zone in the centre, surrounding the wick, consisting of unburnt gas—a luminous cone surrounding this nucleus, consisting of the gases in a state of incomplete combustion. Exterior to this is a thin, non-luminous envelope, where, with a full supply of oxygen, complete combustion is taking place: here we find the hottest part of the flame. The non-luminous or outer part is called the **oxidizing flame**; the luminous part, consisting of carbon and unconsumed hydrocarbons, is called the **reducing flame**.

**946.** *The flame produced by the Blow-pipe* is divided into two parts—the oxidizing flame, where there is an excess of oxygen, corresponding to the outer zone of the candle-flame, and the reducing flame, where there is an excess of carbon, corresponding to the inner zone of the candle-flame. Upon the student's skill in producing these flames, depend very largely the results in the use of the blow-pipe.

In order to produce a good **oxidizing flame**, the jet of the blow-pipe is placed just within the flame, and a moderate blast applied—the air being thoroughly mixed with the gas, the inner blue flame, corresponding to the exterior part of the candle-flame, is produced: the hottest and most effective part is just before the apex of the blue cone, where combustion is most complete.

The **reducing flame** is produced by placing the blow-pipe just at the edge of the flame, a little above the slit, and directing the blast of air a little higher than for the oxidizing flame. The flame assumes the shape of a non-luminous cone, surrounded by a pale-blue mantle; the most active part of the flame is somewhat beyond the apex of the luminous cone.

**947.** The blast with the blow-pipe is not produced by the lungs, but by the action of the muscles of the cheek alone. In order to obtain a better knowledge of the management of the flame, and to practise in producing a good reducing flame, it is well to fuse a small grain of metallic tin upon charcoal, and raising to a high heat endeavor to prevent its oxidation, and keep its surface bright; or better, perhaps, to dissolve a speck of manganese dioxide in the borax bead on platinum wire—the bead becoming amethyst-red in the outer flame and colorless in the reducing flame. The beginner should work only with substances of a known composition, and not attempt the analysis of unknown complex substances, until he has made himself perfectly familiar with the reactions of at least the more frequently occurring elements.

The amount of substance taken for analysis should not be too large; a quantity of about the bulk of a mustard-seed being, in most cases, quite sufficient.

The physical properties of the substance under examination are to be first noted—such as color, structure, odor, lustre, density, etc.

### Heating in Glass Tube Closed at One End.

**948.** The substance, in fragments or in the form of a powder, is introduced into a small glass tube, sealed at one end, or into a small matrass, and heat applied gently, gradually raising it to redness, if necessary with the aid of the blow-pipe. When the substance is in the form of a powder it is more easily introduced into the tube by placing the powder in a narrow strip of paper, folded lengthwise in the shape of a trough; the paper is now inserted into the tube held horizontally, the whole brought to a vertical position, and the paper withdrawn; in this way the powder is all deposited at the bottom of the tube. By this treatment in the glass tube, we are first to notice whether the substance undergoes a change, and whether this change occurs with or without decomposition. The sublimates, which may be formed in the upper part of the tube, are especially to be noted. Escaping gases or vapors should be tested as to their alkalinity or acidity, by small strips of red and blue litmus inserted in the neck of the tube.

### Heat in Glass Tube Open at Both Ends.

**949.** The substance is inserted into a glass tube from two to three inches long, about one inch from the end—at which point a bend is sometimes made; heat is applied gently at first, the force of the air-current passing through the tube being regulated by inclin-

ing the tube at different angles. Many substances undergoing no change in the closed tube, absorb oxygen, and yield volatile acids or metallic oxides. As in the previous case, the nature of the sublimate and the odor of the escaping gas are particularly to be noted. The reactions of sulphur, arsenic, antimony, and selenium, are very characteristic; these metals, if present, are generally easily detected in this way.

### Heat in the Blow-pipe Flame on Charcoal.

950. For this test, a well-burned piece of charcoal is selected, and a small cavity made in that side of the coal showing the annular rings; a small fragment of the substance is placed in the cavity, and, if the substance be a powder, it may be moistened with a drop of water. The coal is held horizontally, and the flame made to play upon the assay at an angle of about twenty-five degrees. The substance is brought to a moderate heat, and finally to intense ignition. Any escaping gases are to be tested for their odor; the change of color which the substance undergoes, and the nature and color of the coating which may form near the assay, are also to be carefully noted. Some substances, as lead, may be detected at once by the nature of the coating.

### Ignition of the Substance previously Moistened with a Drop of Cobalt Nitrate.

951. This test may be effected either by heating on charcoal, in the loop of platinum wire, or in the platinum-pointed forceps. A portion of the substance is moistened with a drop of the reagent, and exposed to the action of the outer flame. When the substance is in fragments, and porous enough to absorb the cobalt solution, it may be held in the platinum-pointed forceps, and ignited. The color is to be noted after fusion. This test is rather limited; Aluminium, Zinc, and Magnesium giving the most characteristic reactions.

### Fusion with Sodium Carbonate on Charcoal.

952. The powdered substance to be tested is mixed with the Soda, moistened, and placed in the cavity of the coal. Some substances form, with soda at a high heat, fusible compounds—others infusible. Many bodies, as silicates, require fusion with alkali carbonate before they can be tested in the wet way. Many metallic oxides are reduced to metal, forming globules, which may be easily detected.

When this test is applied for the detection of sulphates and sulphides, the flame of the alcohol-lamp is to be substituted for that of the gas-flame, as the latter generally contains sulphur compounds.

### Examination of the Color which may be imparted to the Outer Flame.

953. In this way many substances may be definitely detected. The test may be applied either on charcoal or on the loop of platinum wire—preferably in the latter way. When the substance will admit a small fragment is placed in the loop of the platinum wire, or held in the platinum-pointed forceps, and the point of the blue flame directed upon it. If the substance is a powder it may be made into a paste with a drop of water, and placed in the cavity of the charcoal, the flame being directed horizontally across the coal. The color which the substance imparts to the outer flame in either case is noted. In most cases the flame of the Bunsen Burner alone will suffice; the substance being

heated in the loop of platinum wire—which, in all cases, should be first dipped in hydrochloric acid, and ignited, in order to secure against the presence of foreign substances. Those salts which are more volatile at the temperature of the flame, as a rule give the most intense coloration. When two or more substances are found together, it is sometimes the case that one of them masks the color of all the others—the bright yellow flame of Sodium, when present in excess, generally veiling the flame of the other elements. In order to obviate this, Bunsen has furnished us a method,\* by the use of colored media (stained glasses, indigo solution, etc.) The appearance of the flame of various bodies, when viewed through these media, enables us often to detect very small quantities of them in the presence of large quantities of other substances.

### Treatment of the Substance with Borax and Microcosmic Salt.

**954.** This is best effected in the loop of platinum wire. This is heated and dipped into the borax or salt of phosphorus, and heated to a colorless bead: a small quantity of the substance under examination is now brought in contact with the hot bead, and heated, in both the oxidizing and reducing flames. Any reaction which takes place during the heating must be noticed; most of the metallic oxides are dissolved in the bead, and form a colored glass, the color of which is to be observed, both while hot and cold. The color of the bead varies in intensity, according to the amount of the substance used; a very small quantity will, in most cases, suffice. Certain bodies, as the alkaline earths, dissolve in borax, forming beads which, up to a certain degree of saturation, are clear. When these beads are brought into the reducing flame, and an intermittent blast used, they become opaque. This operation is called **flaming**.

As reducing agents, certain metals are employed in the bead of borax or salt of phosphorus. For this purpose **Tin** is generally chosen—Lead and Silver being taken in some cases. These metals cannot be used in the loop of platinum wire, as they will alloy the platinum. The beads are first formed in the loop of wire; then, while hot, shaken off into a porcelain dish, several being so obtained. A number of these are now taken on charcoal and fused into a large bead, which is charged with the substance to be tested, and then with the tin or other metal. For this purpose tin foil (or lead foil) is previously cut in strips half an inch wide, and the strips rolled into rods. The end of the rod is touched to the hot bead to obtain as much of the metal as required. Lead may be added as precipitated lead (“proof-lead”), and silver as precipitated silver. By aid of tin in the bead, cuprous oxide, ferrous oxide, and metallic antimony are obtained and other reductions effected, as directed in 348 and elsewhere.

\* For a full account of the method of analysis by flame reactions and colored media, suggested by CARTMELL; and by films on porcelain, as developed by BUNSEN; consult *Watts' Dict.*, 1st Supplement, p. 125; also *Plattner's Manual, Blow-pipe Anal.*, Richter, N. Y.



TABLE I.

## 955. PRELIMINARY EXAMINATION OF SOLIDS.

*Note physical properties, such as Structure, Gravity, Color, Odor, etc.*

I. Heat a portion, finely pulverized, in a Dry Glass Tube closed at one end (948).

1. *The Substance suffers no change:*

**Absence** of volatile bodies (including combined water), of organic compounds, and of those which change color on heating.

2. *The Substance changes color:*

**Organic compounds** *blacken* from separation of carbon, which burns away.

**Cu** and **Co** salts *blacken* at high heat.

**ZnO** and most **Zn** salts, *yellow while hot, white when cold.*

**PbO** and **Pb** salts, *yellow while hot, yellow when cold.*

**Bi<sub>2</sub>O<sub>3</sub>** (white) and many **Bi** salts, *orange to red-brown while hot, pale-yellow when cold.*

**Fe<sub>2</sub>O<sub>3</sub>**, and salts, *red to black while hot, reddish-brown when cold.*

**Cd(OH)<sub>2</sub>**, and many **Cd** salts, *brown while hot, brown when cold.*

**SnO<sub>2</sub>**, *brown while hot, yellow when cold.*

3. *The substance fuses:*

Most **alkali** salts and numerous other salts. Many salts dissolve in their water of crystallization when heated, becoming solid again by vaporization.

4. *The substance sublimes, partially or wholly:*

**H<sub>2</sub>O** of crystallization, combination, or absorption.

**Sublimate condensing in cold part of the tube.**

**Hg** (449), *gray*, easily rubbed to globules.

**HgCl<sub>2</sub>**, first melts, then forms *white* crystalline sublimate.

**Hg<sub>2</sub>Cl<sub>2</sub>**, without melting, forms a sublimate, *yellow while hot, white when cold.*

**HgS**, a *black* sublimate, turning red on trituration.

TABLE I.—Continued.

<p><b>As</b>, steel gray sublimate ; <i>garlic odor</i>.  <b>As<sub>2</sub>O<sub>3</sub></b> sublimes in <i>white</i> octahedral crystals, does not fuse (472).  <b>As<sub>2</sub>S<sub>3</sub></b>, sublimate nearly <i>black white hot</i>, <i>reddish-yellow when cold</i>.  <b>Sb<sub>2</sub>S<sub>3</sub></b> fuses yellow ; forms <i>white</i>, amorphous sublimes.  <b>NH<sub>4</sub></b> salts, those not decomposing, <i>white</i> sublimate (46).  <b>FeCl<sub>3</sub></b> slowly sublimes as a reddish-yellow stain (320).  <b>S</b>, free or by reduction of sulphide, gives reddish-brown drops, yellow when solidified.  <b>H<sub>2</sub>C<sub>2</sub>O<sub>4</sub></b>, a heavy white vapor and <i>crystalline</i> sublimate.  <b>I</b>, a violet vapor and <i>blue-black</i> sublimate.</p>	<p>5. <i>The substance evolves a gas or vapor :</i></p> <p><b>O</b> indicates the presence of a <b>nitrate</b>, <b>chlorate</b>, <b>bromate</b>, <b>iodate</b>, or <b>peroxide</b>. A small piece of coal placed upon the assay glows upon being heated.</p> <p><b>H<sub>2</sub>S</b>, from hydrated <b>sulphides</b>, some <b>sulphites</b>, blackens <i>lead-paper</i>. Recognized by its odor.</p> <p><b>SO<sub>2</sub></b>, from <b>sulphites</b>, <b>thiosulphates</b>, certain <b>sulphates</b>, etc. Recognized by its odor and bleaching effect.</p> <p><b>NH<sub>3</sub></b>, from its compounds which decompose (46), <i>odor</i>, and alkaline reaction on <i>litmus</i>.</p> <p><b>CN</b>, recognized by characteristic <i>odor</i> and <i>violet flame</i>.</p> <p><b>Oxides of Nitrogen</b>, from <b>nitrates</b> or <b>nitrites</b>, <i>reddish-brown, acrid vapor</i>.</p> <p><b>Acetone</b>, from <b>acetates</b>, characteristic fragrant odor.</p>
<p><b>II. Heat in a Glass Tube open at both ends (949).</b></p>	<p>Certain of the changes stated above as occurring in operation I. are modified by oxidation. Oxides are obtained from metals.</p> <p><b>S and Sulphides</b> yield <b>SO<sub>2</sub></b>. Recognized by its odor and action on litmus-paper.</p> <p><b>As</b> yields a sublimate of <b>As<sub>2</sub>O<sub>3</sub></b>.</p> <p><b>Sb</b> yields a sublimate (white), of <b>Sb<sub>2</sub>O<sub>3</sub></b> and <b>Sb<sub>2</sub>O<sub>5</sub></b>.</p> <p><b>Bi</b>, a sublimate, dark-brown while hot, lemon-yellow when cold (<b>Bi<sub>2</sub>O<sub>3</sub></b>).</p> <p><b>Te</b>, gray sublimate of <b>tellurous acid (TeO<sub>2</sub>)</b>.</p> <p><b>Se</b> and <b>Selenides</b> evolve <b>SeO<sub>2</sub></b>, odor resembling that of rotten horse-radish (612).</p> <p><b>Hg</b>, sublimate of metallic mercury.</p>

### III. Heat in the Blow-pipe! 1. *The substance decrepitates:* Flame on Charcoal (950).

Crystals containing water, as **NaCl**. (If finely pulverized, the decrepitation is avoided.)

#### 2. *The substance deflagrates:*

**Nitrates, Chlorates, Iodates, Hypophosphites, Permanganates**, etc.

#### 3. *The substance fuses, and is absorbed by the charcoal:*

**Salts of alkalis** and some salts of alkaline earths.

#### 4. *The substance is infusible and phosphorescent:*

**Ba, Sr, Ca, Mg**—the residue is alkaline to test-paper.

**Al<sub>2</sub>O<sub>3</sub>, MgO, ZnO** (yellow while hot), not alkaline to test-paper.

#### 5. *The substance forms an incrustation on charcoal:*

**Pb**, lemon-yellow while hot, sulphur-yellow when cold. In thin layers, bluish-white, volatile with bluish flame.

**Bi**, dark orange-yellow while hot, lemon-yellow when cold.

**Zn**, yellow while hot, white when cold, greenish-white flame.

**Cd**, red brown, volatile, dark-yellow flame.

**As**, white. Readily volatilized, distant from the assay, faint blue flame.

**Sb**, white, pale-green flame.

**Sn**, faint-yellow while hot, white when cold.

#### 1. *The mass or incrustation is colored:*

**ZnO**—yellowish-green.

**SnO**—bluish-green.

**Sb<sub>2</sub>O<sub>3</sub>**—dirty dark-green.

**Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, phosphates**—blue.

**MgO**—flesh-color or pink.

**BaO**—brick red.

**SrO, CaO**—gray.

### IV. The Substance (or incrustation of Test III., 5) is moistened with solution Cobalt Nitrate and strongly ignited (951).

TABLE I.—Continued.

<p><b>V. Heat with <math>\text{Na}_2\text{CO}_3</math>, on charcoal in the inner Blow-pipe Flame (952).</b></p>	<p>1. <i>Metallic grains are obtained:</i>  <b>Bi, Sb—brittle.</b>  <b>Pb, Cu, Sn, Au—malleable.</b></p> <p>2. <i>An infusible magnetic powder is obtained:</i>  <b>Fe, Ni, Co.</b></p>
<p><b>VI. Heated in the Blow-pipe Flame, or in the Bunsen Flame on Charcoal, or in a loop of platinum wire (953).</b></p>	<p>1. <i>The substance colors the outer flame:</i>          (If Test V. does not reduce metal, heat on <i>platinum wire</i> for flame color, before the blow-pipe or in Bunsen's flame.)  <i>Yellow</i>: <b>Na</b> and its salts, even in small quantities, impart an intense reddish-yellow. Other salts, even in large quantities, do not interfere with this reaction; viewed through a green glass, appears orange-yellow; moistened with sulphuric acid, the test is more delicate (30).  <i>Violet</i>: <b>K</b> and most of its salts, except borates, phosphates, and silicates, give bluish-violet flame, distinguished in presence of very small quantities of sodium compounds. Excess of the latter prevents the reaction; <b>Li</b> also masks the reaction. In presence of sodium, the potassium flame appears reddish-violet when viewed through a blue glass (20).  <i>Red</i>: <b>Ca</b> and its compounds produce a yellowish-red flame (139).  <b>Sr</b> and many of its salts yield a crimson flame, masked by much <b>Ba</b> (122).  <b>Li</b> and its salts produce a carmine-red flame (55). Sodium interferes with the reaction; Potassium does not.  <i>Green</i>: Yellowish-green—<b>Ba</b> and most of its salts. Also, <b>Mo</b> and its compounds.          Emerald-green—<b>Cu</b> and most of its compounds (349).          Bluish-green—<b>B<sub>2</sub>O<sub>3</sub></b> and <b>phosphates</b>.          Yellowish-green—<b>B<sub>2</sub>O<sub>3</sub></b>, best obtained by the addition of sulphuric acid. Heat on platinum wire until the sulphuric acid is expelled, then moisten with glycerine and ignite (928).          Whitish-green—<b>Zn</b>.  <i>Blue</i>: Light blue—<b>As</b> and many arsenic compounds.          Azure-blue—<b>Pb, Se</b>. Also, <b>CuCl<sub>2</sub></b>.          Greenish-blue—<b>Sb, CuBr<sub>2</sub></b>.</p>



## 956. BEHAVIOR OF SUBSTANCES BEFORE THE BLOW-PIPE WITH MICROCOSMIC SALT AND BORAX.

A clear bead is formed by fusing the flux on a loop of platinum wire. Dip the bead in the finely powdered substance to be examined, and heat again—first, in the oxidizing flame; second, in the reducing or inner flame. Metallic salts are mostly changed to oxides.

In the Table—*h.* signifies hot; *c.*, cold; *sup.*, supersaturated with oxide; *s.*, strongly saturated; *h. c.*, hot and cold.

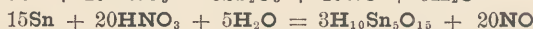
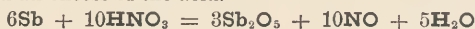
Color of the Bead.	With Microcosmic Salt or Phosphate of Ammonium-sodium.		With Sodium Pyroborate (Borax).	
	In outer or oxidizing Flame.	In inner or reducing Flame.	In outer or oxidizing Flame.	In inner or reducing Flame.
Colorless.	Si (swims undissolved). Al, Mg, Ca, Sr, Ba, Sn, ( <i>g. s.</i> , opaque). Ti, Zn, Cd, Pb, Bi, Sb, ( <i>viol. sat.</i> )	Si (swims undissolved). Al, Mg, Ca, Sr, Ba, ( <i>sup.</i> , not clear). Co, Mn, Sn.	<i>h. c.</i> : Si, Al, Sn. ( <i>sup.</i> , opaque). Al, Mg, Sr, Ca, Ba, Ag, ( <i>not sat.</i> ) Zn, Cd, Pb, Bi, Sb, Ti, Mo.	Si, Al, Sn, ( <i>g. s.</i> , opaque). Alkaline earths and earths. <i>h. c.</i> : Mn, Co. <i>h.</i> : Cu.
Yellow or Brownish.	<i>h.</i> ( <i>g. s.</i> ): Fe, Ur, Ce. <i>c.</i> : Ni.	<i>h.</i> : Fe, Ti. <i>c.</i> : Ni.	<i>h.</i> , <i>not sat.</i> : Fe, Ur. <i>h.</i> , <i>sup.</i> : Pb, Bi, Sb.	<i>h.</i> : Ti, Mo.
Red.	<i>h.</i> ( <i>g. s.</i> ): Fe, Ni, Cr, Co.	<i>c.</i> : Cu. <i>h.</i> : Ni, Ti with Fe.	<i>h.</i> : Fe, Co. <i>c.</i> : Ni.	<i>c.</i> : Cu ( <i>sup.</i> , opaque).
Violet or Amethyst.	<i>h.</i> , <i>c.</i> : Mn.	<i>c.</i> : Ti.	<i>h. c.</i> : Mn. <i>h.</i> : Ni with Co.	<i>c.</i> : Ti.
Blue.	<i>h.</i> , <i>c.</i> : Co. <i>c.</i> : Cu.	<i>h.</i> , <i>c.</i> : Co. <i>c.</i> : W.	<i>h. c.</i> : Co. <i>c.</i> : Cu.	<i>h. c.</i> : Co.
Green.	<i>h.</i> : Cu, Mo; Fe with Co or Cu. <i>c.</i> : Cr.	<i>c.</i> : Cr. <i>h.</i> : Ur, Mo.	<i>c.</i> : Cr. <i>h.</i> : Cu, Fe with Co.	Cr. <i>sup.</i> : Fe.
Gray and Opaque.		Ag, Pb, Sb, Cd, Bi, Zn, Ni.		The same as with Microcosmic salt.

## TREATMENT OF A METAL OR AN ALLOY.\*

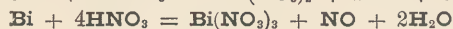
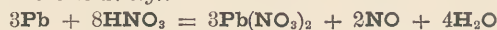
957. On account of the different effect that Nitric Acid has upon the uncombined metals, it is used as a solvent in their detection. Thus :

*Gold* and *Platinum* are not attacked by Nitric Acid.

*Tin* and *Antimony* are oxidized and converted into compounds that are insoluble both in water and an excess of the acid.



*All the other metals* are oxidized and converted into compounds that dissolve either in water or an excess of the acid: *e.g.*:

*Method of Procedure.*†

Place a small quantity of the metal or alloy, about equal in bulk to a pea, having previously obtained it in as finely divided a state as possible, in an evaporating-dish, or any suitable vessel, cover well with Nitric Acid, *sp. gr.* 1.20, and apply heat. Continue the application of heat, replacing from time to time the acid lost by evaporation, until the metal or alloy is dissolved or wholly disintegrated.

If complete solution takes place immediately, pass on to *A*.

If a residue remains decant the liquid portion upon a filter; again add Nitric Acid to the residue, heat, and again decant upon the same filter. Then thoroughly wash with hot water, either by boiling with water and decanting, or by transferring the whole to and pouring hot water through the filter. Add the first portions of the hot-water filtrate to the Nitric Acid filtrate already obtained, and treat the mixture as directed in *A*, after having, first, evaporated a drop or two on platinum foil, to ascertain whether anything has really been dissolved.

Treat the residue as directed in *B*.

*A.—The Nitric Acid Solution.*

This solution may contain any of the metals, except those mentioned under *B*.

If the Nitric Acid has effected a whole or partial solution of the original metal or alloy, evaporate almost to dryness to remove excess of acid, add about ten times its bulk of water, and proceed with the separation and detection of the metals in the regular way.

Should the concentrated liquid become turbid when diluted with water, the presence of bismuth is indicated. In this case enough acid must be added to clear up the solution.‡

\* This section is furnished by J. W. Baird, A.M., Professor of Analytical Chemistry in the Massachusetts College of Pharmacy, recently Instructor in Assaying and Qualitative Analysis in Lehigh University.

† When gold or platinum constitutes more than one-quarter of the alloy, Nitric Acid fails to extract the whole of the base metals that otherwise are readily soluble. In such a case the amount of gold or platinum must be reduced to at least 25 per cent. by fusing the alloy with the requisite amount of that base metal whose absence is surely known.

‡ Arsenic, if present in the original alloy, now exists in the form of Arsenic Acid, the precipitation of which requires heat and long-continued passage of  $\text{H}_2\text{S}$ .

*B.—The Residue Insoluble in Nitric Acid.*

This may contain gold and platinum in their metallic forms, and tin\* and antimony\* in the form of metastannic and antimonie acids. The separation of the two former from the two latter depends upon the fact that the metastannic and antimonie acids are soluble in hydrochloric acid, forming  $\text{SnCl}_4$  and  $\text{SbCl}_5$ .

Digest, therefore, the well-washed residue in concentrated hydrochloric acid at a boiling temperature for from 5 to 10 minutes; then add at once an equal volume of water (to take the  $\text{SnCl}_4$  into solution), and bring to the boiling point.

If gold or platinum existed in the original metal or alloy it will now be found in the form of a dark-brown or black powder or mass, insoluble in the hydrochloric acid. If such a residue exists, *decant while hot*, again add hydrochloric acid, heat, and again *decant*.

*The Hydrochloric Acid Solution.*

This solution may have a turbid appearance, especially when cold, due to the action of the water upon the  $\text{SbCl}_5$ ; but without filtering proceed with the separation and detection of the tin and antimony by the usual process.†

*The Dark-Colored Residue.*

Add, after washing, two volumes of hydrochloric and one of nitric acid; evaporate almost or quite to dryness, dissolve in a small quantity of water (to obtain a concentrated solution), and divide into two portions.

The gold and platinum have been dissolved by the aqua-regia formed, and now exist as auric and platinic chlorides.

*First Portion—Test for Gold.*

Dilute with at least ten times its bulk of water; add a drop or two of a mixture of stannous and stannic chlorides; a purple or brownish-red precipitate (or coloration), purple of cassius, constitutes the test for gold.

A convenient way of preparing this mixture of stannous and stannic chlorides is to

(a) Add a few drops of chlorine-water to a solution of stannous chloride; or

(b) Add to a small quantity of stannous chloride enough ferric chloride to produce a faint coloration.

*Second Portion—Test for Platinum.*

Add, without dilution, an equal volume of a strong solution of ammonium chloride. The formation, either at first or on standing, of a lemon-yellow crystalline precipitate, consisting of the double chloride of platinum and ammonium— $(\text{NH}_4\text{Cl})_2\text{PtCl}_4$ —constitutes the test for platinum.

Addition of alcohol favors the precipitation.

If the proportion of platinum is very small, the mixture, after ammonium chloride has been added, should be evaporated to dryness on a water-bath and the residue treated with dilute alcohol. The ammonium platinic chloride remains behind as a yellow crystalline powder.

\* Traces may sometimes be dissolved.

† Arsenic must be looked for in this as well as in the nitric acid solution. For when the alloy contains arsenic, part of it will combine with the antimony and tin, and be held in the residue.





*The Precipitate is washed on the filter with one or two small portions of cold water; then treated with much hot water, and filtered.*

<p><b>Solution: <math>\text{PbCl}_2</math>, (900).</b></p> <p><i>Test for Lead (549) by</i></p> <p><b>Sulphuric acid</b>, giving <math>\text{PbSO}_4</math>, <i>white</i>.</p> <p><b>Hydrosulphuric acid</b>, <math>\text{PbS}</math>, <i>black</i>.</p> <p><b>Chromate</b>..... <math>\text{PbCrO}_4</math>, <i>yellow</i>.</p> <p><b>Iodides</b>..... <math>\text{PbI}_2</math>, (392).</p> <p>The precipitates may be tested by the blow-pipe (397 and 398).</p>	<p><b>Remaining Precipitate: <math>\text{AgCl}</math>, <math>\text{Hg}_2\text{Cl}_2</math>.</b></p> <p><i>Digest with dilute, warm Ammonium Hydroxide, and filter.</i></p> <p><b>Solution: <math>(\text{NH}_4)_2(\text{AgCl})_2</math>.</b></p> <p><i>Test for silver (550), after expelling any excess of ammonium hydroxide by boiling, by acidulating slightly with nitric acid. A precipitate is <math>\text{AgCl}</math>.</i></p> <p>For other tests, the silver chloride may be reduced to the metal by <b>zinc</b> (420), or on <b>charcoal</b> before the blow pipe (422), and the metal dissolved by <b>nitric acid</b> (407), the resulting solution giving all the reactions of silver.</p> <p>If the original solution does not contain non-alkali metals, it may be used to obtain the characteristics of silver.</p>	<p><b>Residue: <math>\text{NH}_4\text{Hg}_2\text{Cl}</math>, black (433).</b></p> <p>[Lead Oxychloride, <i>white</i>, 548.]</p> <p>The black color is the evidence of mercury. Additional proof may be obtained by testing the residue, or a portion of it, for mercury by drying and heating with <b>sodium carbonate</b>, in a glass tube (449).</p> <p>For reactions of mercury in solution, if the original solution contains non-alkali metals, dissolve the residue with <b>nitro-hydrochloric acid</b>—as mercuric chloride.</p>
<p><i>For the study of lead, see the Table at 452 and the text at 387.</i></p>	<p><i>Follow the Table at 452, and refer to the text at 411,</i></p>	<p><i>Follow 452, and refer to the text at 346. Also see 960 "B."</i></p>

## 960. ANALYSIS OF GROUP II. (Explanation at 555.)

Wash the precipitate thoroughly on the filter, and then digest (in the test-tube) with yellow ammonium sulphide,\* using as little as possible. Treat the Residue, well-washed, as directed in "B." Precipitate the Filtrate with dilute hydrochloric acid (diluting with solution of hydrosulphuric acid), and filter; examining this Precipitate,† when washed, for As, Sb, Sn, according to "A." [For Gold, 580; Platinum, 589; Rare Metals, 593 to 612.]

"A." Precipitate from the Ammonium Sulphide Solution :  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}_2$ , ( $\text{S}_2$ ).

Treat the washed precipitate with hydrochloric acid, and, if it does not dissolve, add a minute fragment of potassium chlorate, and digest in a test-tube, till the sulphides are dissolved (or decolorized). Filter out any sulphur, washing the filter with a few drops of hydrochloric acid, and receiving the filtrate in an evaporating-dish. Remove all the chlorine by a very gentle heat, until wet litmus-paper is not bleached by the vapor. Transfer to the Generator of a Marsh's Apparatus (carefully rinsing in any white residue of antimony or tin oxides) (558).

Solution : ‡  $\text{H}_3\text{AsO}_4$ ,  $\text{SbCl}_5$ ,  $\text{SnCl}_4$ .

Place in the Generator sufficient zinc (a piece of platinum foil or wire, 288) and dilute sulphuric acid (or use Na-amalgam, Al, or Mg, 463 and 534), and receive the gas in solution of silver nitrate (as long as a precipitate is produced). Now filter, and wash the residue.

In the Generator : Sn, (Sb, Zn salt).

Gather and wash the solid contents of the generator; dissolve with moderately dilute hydrochloric acid, as directed in 535. (An undissolved residue may be Sb, soluble in nitro-hydrochloric acid.) Test the solution ( $\text{SnCl}_2$  for tin by  $\text{HgCl}_2$ : a white or gray precipitate (537).

Precipitate, from  $\text{SbH}_3$ :  $\text{Ag}_2\text{Sb}$ , (Ag).

Digest with warm hydrochloric acid to dissolve the antimony (506), dilute (not to precipitate), and test the solution for antimony by—

$\text{H}_2\text{S}$ : an orange precipitate. §

Water: a white precipitate (497).

Spots and Mirror, from  $\text{SbH}_3$  (466).

Solution, from  $\text{AsH}_3$ :  $\text{H}_3\text{AsO}_3$  ( $\text{AgNO}_3$ ,  $\text{HNO}_3$ ).

Remove the silver by adding just enough hydrochloric acid and filtering (409).

Test the solution for arsenic by—

$\text{H}_2\text{S}$ : a yellow precipitate. ||

$\text{AgNO}_3$ : (467).

Spots from the flame (466).

Sublimation from the sulphide (471).

Follow 545, and the text at 539 and after.

Follow 545, and consult the text at 497.

Follow 545, and consult 458 and after.

\* If Copper is present, and Mercury absent, it is better to use sodium sulphide (557).

† A white precipitate, of sulphur, will occur in any case. Colored precipitates indicate As, Sb, or Sn (556).

‡ In many cases, the original solution can be used for additional results through Marsh's Test (463).

§ A black precipitate shows that too much  $\text{HCl}$  was used, and some silver dissolved.

|| A black precipitate shows that too little or too much  $\text{HCl}$  was used.

961. "B." SULPHIDES NOT SOLUBLE IN AMMONIUM SULPHIDE :  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{CdS}$ ,  $\text{HgS}$ .\*

If sulphides have been found in "A," the precipitate should be washed, first with  $(\text{NH}_4)_2\text{S}_2$  (or  $\text{Na}_2\text{S}$ ), then with water. Dissolve the precipitate by action of hot, moderately dilute nitric acid (564). Evaporate the solution to expel excess of nitric acid.

Residue:	Solution: $\text{Pb}(\text{NO}_3)_2$ , $\text{Bi}(\text{NO}_3)_3$ , $\text{Cu}(\text{NO}_3)_2$ , $\text{Cd}(\text{NO}_3)_2$ .		
$\text{HgS}$ , $\text{S}$ [ $\text{PbSO}_4$ ].	To a portion of the solution, add a drop of very dilute sulphuric acid. If a precipitate appears (565), add the reagent to the whole solution, and filter.		
Dissolve the (black) precipitate by nitrohydrochloric acid, and expel free chlorine by boiling (571).	Precipitate: $\text{PbSO}_4$ .	Filtrate: $\text{Bi}$ , $\text{Cu}$ , $\text{Cd}$ , salts. Add ammonium hydroxide to a slight alkaline reaction.	
Solution: $\text{HgCl}_2$ .	Add Chromate, and heat (567). Or add $\text{KI}$ (392).	Precipitate: $\text{Bi}(\text{OH})_3$ .	Blue Solution: Copper (340), cadmium (374). Colorless Solution: Cadmium, absence of copper.
Test for mercury by Stannous chloride (448 a).	(Lead chromate dissolves in potassium hydroxide, and precipitates with acetic acid.)	Filter out and wash the precipitate and test it by stannite, according to 366. Or, test by dissolving with a very little $\text{HCl}$ on a watch-glass and adding water (358).	To the concentrated (acidified or alkaline) solution, add $\text{H}_2\text{S}$ : a yellow precipitate, $\text{CdS}$ . To the neutral solution add $\text{K}_4\text{Fe}(\text{CN})_6$ : $\text{Cd}_2\text{Fe}(\text{CN})_6$ , white. Cyanides (374).
Ammonia (443). Copper (448 d). Sublimation (449).	Test the pre. of sulphates, or sulphide, by reduction on charcoal (397).		
Follow 452, and the text at 442 and after.	See 959. Follow 452, and the text at 387.		For copper, follow 376 and 339. If copper is present, treat the sulphide obtained by adding $\text{H}_2\text{S}$ to the ammoniacal solution, by one of the methods given in 570, for separation of cadmium.
			For Cadmium, see the text at 376

\* If silver was not removed in the first group, it may be tested for, in the nitric solution of this precipitate, by  $\text{HCl}$ .

## 962. ANALYSIS OF GROUP III., IN ABSENCE OF PHOSPHATES.

The Scheme of Separations given in 301 is preferred to this, in most Cases.

To the filtrate from the second group (958), add  $\text{NH}_4\text{OH}$  till alkaline, then add  $\text{NH}_4\text{Cl}$  and Ammonium Sulphide.

Dissolve the well-washed Precipitate, on the Filter, by dilute, cold hydrochloric acid (303). Concentrate in an evaporating-dish.

Solution:  $\text{ZnCl}_2$ ,  $\text{Al}_2\text{Cl}_6$ ,  $\text{FeCl}_2$  (214),  $\text{MnCl}_2$ ,  $\text{Cr}_2\text{Cl}_6$ ,  $\text{NiCl}_2$ ,  $\text{CoCl}_2$ .

Residue:  $\text{CoS}$ ,  $\text{NiS}$ , black. Test black residue by the blow-pipe for cobalt and nickel. Dissolve by nitric acid, and test for **Ni**, by 280. Add potassium hydroxide solution to strong supersaturation and boil a short time (291). Filter, and wash. Separation of **Zn** and **Al**.

Solution:  $\text{K}_2\text{ZnO}_2$ ;  $\text{K}_2\text{Al}_2\text{O}_4$ .

Precipitate:  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}_2(\text{OH})_6$ ,  $\text{Mn}(\text{OH})_2$ ,  $\text{Cr}_2(\text{OH})_6$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$ .

Divide the solution into two portions.

Examine five portions; two in solution (for **Fe** and **Ni**), and three in precipitate (for **Cr**, **Mn**, **Co**).

1. For Zinc.	2. For Aluminium.	1 and 2. For Iron and for Nickel.	3. For Manganese.	4. For Chromium.	5. For Cobalt.
Add ammonium sulphide; a precipitate, $\text{ZnS}$ (294).	Add Ammonium chloride in decided excess (392). A precipitate: $\text{Al}_2(\text{OH})_6$ .	Dissolve with a drop or two of nitro-hydrochloric acid, and expel all free chlorine.	Boil with $\text{PbO}_2$ and $\text{HNO}_3$ , as directed in 248; a red color, $\text{H}_2\text{Mn}_2\text{O}_8$ . Or fuse with $\text{Na}_2\text{CO}_3$ and $\text{KNO}_3$ , as directed in 249; a green mass, manganate, as $\text{K}_2\text{MnO}_4$ .	(If <b>Mn</b> is present, proceed by 301, with the filtrate from 2d group.) Fuse with $\text{Na}_2\text{CO}_3$ and $\text{KNO}_3$ (187), dissolve in water, acidify by acetic acid and test for chromic acid, by 191, 192, 193. Test, also, the original solution for chromic acid (182).	Test in the borax bead (269).
This precipitate may be dissolved by $\text{HCl}$ , or, in absence of interfering bases, the original solution taken, for additional tests for zinc.	Dissolve and test this solution, or test the original solution, if free from interfering bases, for aluminium.	Test a portion for Iron by potassium thiocyanate: a red solution, $\text{Fe}_2(\text{CNS})_6$ .  Test the original solution for Ferrous and Ferric iron by ferrixyanide and thiocyanate, 221.			
	For Iron, follow the test at 204 and after.				
Follow 300, and the test at 292.	Follow 300, and the test at 167.	Test a portion for Nickel, by 280 or 281.	Follow 300, and consult the test at 242 and after.	Follow 300, and the test at 181 and after.	Consult the test at 264.



[The Scheme at 307 may be used instead of this one]

To the Filtrate from Group II., add ammonium chloride, and ammonium hydroxide to alkaline reaction, then ammonium sulphide to complete the precipitation. Reserve the Filtrate for Group IV.

**Precipitate:** FeS, MnS, CoS, NiS, ZnS, S;  $\text{Al}_2(\text{OH})_6$ ,  $\text{Cr}_2(\text{OH})_6$ ; phosphates of Al, Cr, and of Ba, Sr, Ca, Mg.

Treat the well-washed precipitate with cold dilute hydrochloric acid. If a black residue remains, test it for Co and Ni, as directed in the Table at 301 B. Also, this residue may be tested for Si (746). The filtered solution is boiled to expel  $\text{H}_2\text{S}$  filtered if turbid, and a smaller portion reserved.

## Portion 1.

Add a few drops of nitric acid and boil.

**Solution:**  $\text{Fe}_2\text{Cl}_6$ ,  $\text{Al}_2\text{Cl}_6$ ,  $\text{Cr}_2\text{Cl}_6$ ,  $\text{MnCl}_2$ ,  $[\text{CoCl}_2]$ ,  $[\text{NiCl}_2]$ ,  $\text{ZnCl}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $(\text{H}_2\text{SiO}_3)$ ; also Ba, Sr, Ca, Mg, chlorides.

(1) Test a small portion for iron, by thiocyanate. If iron is found, test the original solution by ferricyanide and thiocyanate as directed in 221.

(2) To the remainder, add ferric chloride till a drop is precipitated yellow by ammonium hydroxide (showing that the  $\text{PO}_4$  is all precipitated), concentrate to a small bulk; add water, nearly neutralize by  $\text{K}_2\text{CO}_3$ , and add excess of barium carbonate. Let the mixture stand and filter.

**Precipitate:**  $\text{Al}_2(\text{OH})_6$ ,  $\text{Cr}_2(\text{OH})_6$ ,  $[\text{Fe}_2(\text{PO}_4)_2]$ ,  $\text{Fe}_2(\text{OH})_6$ ,  $\text{BaCO}_3$ .  
Boil the precipitate for some time with sodium or potassium hydroxide.

**Solution**  $\text{K}_2\text{Al}_2\text{O}_4$ .

Acidify the solution with HCl and add excess of ammonium hydroxide, and boil.

**Precipitate:**  $\text{Al}_2(\text{OH})_6$ .

Follow the test at 166.

**Precipitate:**  $\text{Cr}_2(\text{OH})_6$ , etc.

Test for chromium as directed in 301 (p. 70).

## Portion 2.

**Solution:**  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , etc.  
Add sulphuric acid and filter.

**Precipitate:**  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ ,  $(\text{CaSO}_4)$ .

Test the precipitate for Sr, by the flame. [Test it for Ba by fusing with  $\text{K}_2\text{CO}_3$  (823), then dissolving the well-washed residue by acetic acid and obtaining reactions with chromate, etc.] To the filtrate, add alcohol. A precipitate may be  $\text{CaSO}_4$ . Boil with water and add  $\text{NH}_4\text{OH}$  and oxalate, for calcium.

**Solution:**  $\text{MnCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ .

Add HCl and boil to expel  $\text{CO}_2$ . Add  $\text{NH}_4\text{OH}$  to alkaline reaction, then ammonium sulphide, and warm and filter.

**Precipitate:**  $\text{MnS}$ ,  $\text{ZnS}$ .

Dissolve by HCl\* and test the solution ( $\text{MnCl}_2$ ,  $\text{ZnCl}_2$ ) by the directions in 301 (B), p. 70. [Or separate by Acetic Acid, 293.]

**Filtrate:**  $\text{BaCl}_2$ ,  $\text{MgCl}_2$ .

Remove Ba, Sr, Ca, by adding  $\text{H}_2\text{SO}_4$ , as directed in Portion 2, above, then add ammonium oxalate and hydroxide, filter, and test the filtrate for Mg, by adding phosphate.

\* If a black residue appear, test for cobalt and nickel, as directed in foot-note 301 B.

## 964. ANALYSIS OF GROUP IV. (Explanation in 142.)

[The Method of Separation given in 146 may be used instead of this.]

[Concerning the loss of traces of barium and calcium, see 144.]

*Dissolve the well-washed precipitate in dilute acetic acid. Solution:  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ .*

*To a small portion of the solution, add potassium dichromate; if a precipitate appears, add the reagent to the whole solution as long as a precipitate is produced (105), and filter.*

<p><b>Precipitate:</b> <math>\text{BaCrO}_4</math>, yellow.</p> <p><i>The precipitate is soluble by hydrochloric acid, and this solution is precipitated by sulphuric acid, as <math>\text{BaSO}_4</math>, insoluble in acids.</i></p>	<p><b>Solution:</b> <math>\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2</math>, <math>\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2</math>, <math>[\text{K}_2\text{Cr}_2\text{O}_7]</math>.</p> <p><i>Precipitate by ammonium carbonate with ammonium hydroxide; filter, and wash the precipitate, and dissolve it by acetic acid.</i></p> <p><b>Solution:</b> <math>\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2</math>, <math>\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2</math>. <i>Divide in two portions.</i></p>				
<p><i>See 100 and after.</i></p>	<table border="1"> <thead> <tr> <th data-bbox="640 635 885 1105">For Strontium :</th><th data-bbox="640 171 885 635">For Calcium :</th></tr> </thead> <tbody> <tr> <td data-bbox="640 635 885 1105"> <p><i>To a portion, add solution of calcium sulphate; boil, and leave for about ten minutes. A precipitate indicates strontium, <math>\text{SrSO}_4</math>.</i></p> <p><i>Test another portion of the solution on a loop of platinum wire, by the flame (955 VI.)</i></p> </td><td data-bbox="640 171 885 635"> <p><i>Add solution of potassium sulphate (and filter), to insure the absence of strontium.</i></p> <p><i>To the filtrate (or solution not precipitated), add ammonium oxalate. A precipitate: <math>\text{CaC}_2\text{O}_4</math>, insoluble in acetic acid, soluble in hydrochloric.</i></p> <p><i>Test by the flame (955 VI.)</i></p> </td></tr> </tbody> </table>	For Strontium :	For Calcium :	<p><i>To a portion, add solution of calcium sulphate; boil, and leave for about ten minutes. A precipitate indicates strontium, <math>\text{SrSO}_4</math>.</i></p> <p><i>Test another portion of the solution on a loop of platinum wire, by the flame (955 VI.)</i></p>	<p><i>Add solution of potassium sulphate (and filter), to insure the absence of strontium.</i></p> <p><i>To the filtrate (or solution not precipitated), add ammonium oxalate. A precipitate: <math>\text{CaC}_2\text{O}_4</math>, insoluble in acetic acid, soluble in hydrochloric.</i></p> <p><i>Test by the flame (955 VI.)</i></p>
For Strontium :	For Calcium :				
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<p><i>See the text at 120.</i></p>	<p><i>Follow the text from 132 to 140.</i></p>				

Evaporate a drop or two on clean platinum foil by a gentle heat (9). If a residue is obtained, ignite. If the residue or a part of it vaporizes immediately, ammonium compounds are indicated. (The melting of fixed alkali salts is liable to be mistaken for vaporization.)

<p><b>For Ammonium</b>, test a portion of the original material with calcium, or potassium, or sodium hydroxide, at a gentle heat. The vapor of ammonia, <math>\text{NH}_3</math>, is recognized by its effect on moistened litmus-paper, its odor, etc. (39). Conduct the gas into water, and add potassium mercuric iodide with <math>\text{KOH}</math> (40). Test another portion of the same solution by <math>\text{HgCl}_2</math> (41). If no interfering acids or bases are present, the <math>\text{K}_2\text{HgI}_4</math> with <math>\text{KOH}</math> may be added to the original solution.</p>	<p><b>For Magnesium</b>, test the Filtrate from Group IV. Add a little ammonium hydroxide; then enough ammonium chloride to dissolve any precipitate which appears (79), and then sodium phosphate. Precipitate: <math>\text{MgNH}_4\text{PO}_4</math>. Concerning lithium phosphate, see 53. Calcium, in traces, may appear here, as phosphate (144). To guard against this fallacy, add oxalate to the filtrate from the fourth group, and filter out any precipitate so made.</p>	<p>If magnesium is present, its compounds lessen the delicacy of the Flame Tests for the Metals of the Alkalies, and wholly prevent tests by precipitation. To remove Magnesium, precipitate it by barium hydroxide and then remove the barium, as directed in 150.</p>	<p><b>For Potassium</b>, test by the flame (on platinum wire, with the Bunsen burner); violet, not obscured by blue glass (20). Test by Tartaric acid, using a concentrated solution.</p>	<p><b>For Sodium</b>, test (on platinum wire) for the flame color, yellow, and given by extraneous traces of sodium compounds (32). Obscured by the blue glass.</p>	<p><b>For Lithium</b>, test by the flame, crimson, and obscured only by very thick blue glass (55). Test by sodium phosphate. The precipitate, <math>\text{Li}_3\text{PO}_4</math>, is soluble in much ammonium chloride (distinction from magnesium).</p>
<p>Consult 35 to 47.</p>	<p>Follow the test at 76 and after.</p>	<p>Follow the test at 16 to 21, and 953. (See 955.)</p>	<p>Follow the text at 28 and after, and 955 VI.</p>		

## 966. PRELIMINARY EXAMINATION FOR ACIDS.

Concerning the indications of acids in the Blow-pipe Examination, see 931 and 955; the indications in dissolving Solids, see 932; the considerations relative to any Bases already determined, see 933; the Removal of Bases, see 934-936; Reactions in the Wet Way, see 967, 968.

<p><b>For the Vaporous Acids:</b> If the vapor reddens moist blue litmus-paper, some one or more of the following-named volatile acids is indicated:</p> <p><b>I. To a little of the solid substance or residue by evaporation, or very concentrated solution, in a test-tube, add a little concentrated Sulphuric Acid, and heat gently, not enough to vaporize the sulphuric acid.</b></p> <p>For carbonates, sulphides, and cyanides, it is better to add dilute sulphuric acid.</p>	<p><b>For the Vaporous Acids:</b> <i>If the vapor reddens moist blue litmus-paper, some one or more of the following-named volatile acids is indicated:</i></p> <p><b>1. There is sudden effervescence:</b></p> <p>Carbonic anhydride, <math>\text{CO}_2</math>. <i>Colorless and odorless gas, feebly reddening litmus, and making solution of calcium hydroxide turbid. See 665. If the original substance contains non-alkali bases in solution, carbonates cannot be present. Solutions of carbonates give precipitates with salts of all non alkali metals, 667.</i></p> <p>Oxalates (651) and cyanates (696) also evolve <math>\text{CO}_2</math>.</p> <p><b>2. Effervescence of gas having odor:</b></p> <p>Hydrosulphuric acid, <math>\text{H}_2\text{S}</math>. <i>Blackens paper wet with lead acetate. Most sulphides are transposed by hydrochloric acid with evolution of <math>\text{H}_2\text{S}</math>; decomposed by nitric acid or chlorine with separation of S. Sulphides in solution precipitate salts of the first three groups of bases (781). See 779 and test by II.</i></p> <p>Sulphurous anhydride, <math>\text{SO}_2</math>. <i>Odor of burning sulphur. Bleaches litmus. Colors iodic acid and starch (809). Sulphites precipitate salts of all non-alkali bases. Follow the text at 802.</i></p> <p>Thiosulphates, also, evolve sulphurous anhydride, on decomposition—sulphur being separated, 786. Decomposed by all acids. Form precipitates (788), soluble in excess.</p>
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**Hydrocyanic Acid, HCN.** Peach-blossom *odor*. Gas precipitates **silver nitrate**, on a glass rod, as **AgCN**. Change to *thiocyanate*, gives blood-red color with ferric salts (682); to ferrocyanide, gives blue color with iron salts (681). Alkali cyanides are decomposed by all acids. In solution, they precipitate most of the second and third group metals (679).

**Acetic acid,  $H(C_2H_3O_2)$ .** *Odor* of vinegar. Digested with alcohol and sulphuric acid, gives odor of *acetic ether* (636). Acetates are transposed by hydrochloric and nitric acids. In solution, form **no precipitates**, but give red solution with ferric salts (635).

**Hydrochloric acid, HCl.** Slight effervescence. Slight, irritating *odor*. The gas forms a white precipitate (**AgCl**) with solution of **silver nitrate**, on a glass rod; the precipitate being insoluble in dilute nitric acid, but soluble in ammonium hydroxide (843). The gas forms a white cloud with vapor of ammonia. Obtain  **$CrO_2Cl_2$** , by 845. Chlorides precipitate salts of all the **first-group bases** (842). Compare the reactions by **table** at 918. For separations, see 920\* and 928.

### 3. *Appearance of gas having color:*

**Hydriodic acid, HI.** *Odor* is offensive, and slightly chlorine-like. Vapor *colors* violet in the air—both odor and color due to separation of free iodine. Vapor and mixture color **starch** blue. **Carbon disulphide** extracts iodine, violet. Soluble iodides are *transposed* by **HCl** and *decomposed* by **Cl** and by  **$HNO_3$** . In solution, give colored precipitates with salts of the **first-group metals** (see 897 to 903). Compare reactions by **table**, 918. For separations, see 920 and 928.

**Hydrobromic acid, HBr.** *Odor* is acrid and chlorine-like. *Color*, slightly yellowish-brown—odor and color due to separation of free bromine. **Starch** colors yellow;

\* For an application of the chlorochromic test, by Prof. Wiley, see *Chem. News*, xli. 176, April 16, 1890.

Carbon disulphide yellow ; iodine being absent in both tests. Soluble bromides *transposed* by  $\text{HCl}$  and *decomposed* by  $\text{HNO}_3$  and by  $\text{Cl}$ . In solution, give yellowish-white or white precipitates with salts of the first-group bases (872). Compare reactions, by aid of the table at 918. For separations, see 920 and 928.

**Nitrous acid,  $\text{HNO}_2$ , and nitric peroxide,  $\text{NO}_2$ , characteristic acid odor.** *Color,* red-brown. Color potassium iodide and starch, blue. Salts all soluble. See the text at 709.

The brown gas is produced very sparingly from nitrates (unless reducing agents are present), but produced abundantly from nitrites. See special Tests (III.)

**Chloric acid,  $\text{HClO}_3$ .** *Detonation* with sulphuric acid. *Odor* of chlorine. *Color,* greenish-yellow. Gas bleaches litmus. Chlorates decomposed by hydrochloric acid (861) and by nitric acid. By **ignition**, reduced to chlorides. Form **no precipitates**, except by reduction (compare reactions by the table at 918).

**Chlorine,  $\text{Cl}$ ,** is evolved in the decomposition of **hypochlorites** (853), and in that of chlorides with oxidizing agents (844).

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## II. Fuse with pure Sodium Carbonate, on charcoal, and test the mass obtained.

### 1. When moistened, it blackens silver :

Indications of **sulphur** in any combination or uncombined (783).

*Fusion with sodium carbonate on platinum foil or in a porcelain capsule.* The mass blackens silver : a **sulphide**, a **thiosulphate**, or one of the thionates. The mass does not blacken silver : a **sulphate**.

### 2. When acidified with hydrochloric acid, filtered, and the filtrate evaporated to dryness and treated with the same acid, an insoluble residue is obtained: Silicic anhydride, $\text{SiO}_2$ .

Soluble in boiling solutions of fixed alkalis. See 746 and the bead-test (956).

### III. Certain Tests not classified.

#### 1. For Nitric acid and Nitrous acid:

Trial to be made, in case of any material soluble in water (721 and 711). Only slight portions of nitrites could escape recognition by the brown gas evolved in Test I., as above mentioned. Nitrates, with reducing agents, evolve brown gas abundantly, in Test I.

Test for Nitric and nitrous acids, by formation of the "brown ring" (724).  
Tests for Nitrous acid by 710 and 709.

#### 2. For Boric acid:

Borates of non-alkali metals, insoluble (624). See Flame Test, 955 VI. Test by 626 and 628.

#### 3. For Silicic acid:

Compounds insoluble, except those giving a very strong alkaline reaction. See test in the bead, 956. See Test II., 2, above.

#### 4. For Ferrocyanic, Ferricyanic, and Thiocyanic acids:

Heated with sulphuric acid, evolve  $\text{HCN}$  (687).

Thiocyanates, fused with  $\text{KNO}_3$ , form soluble sulphates.

Insoluble salts of  $\text{H}_4\text{Fe}(\text{CN})_6$ , and  $\text{H}_2\text{Fe}_2(\text{CN})_{12}$ , boiled with solution of  $\text{KOH}$ , form soluble potassium salts (677 c).

When in solution, test with iron salts (221).

For solubilities, ferrocyanides, see 689; ferricyanides, 693; thiocyanates, see 700.

The  $\text{CN}$  of single cyanides is separated by slightly acidulating, adding calcium carbonate, and distilling—ferrocyanogen and ferricyanogen and thiocyanogen being retained as salts.

## 967. EXAMINATION FOR THE MORE COMMON NON-VAPOROUS ACIDS, AS BARIUM AND CALCIUM SALTS.

Concerning the Removal of Bases, before Testing for Acids, see 934.

*Heat a portion of the neutralized solution,\* and add both barium chloride and calcium chloride.*

**Precipitate:**  $\text{BaSO}_4$ ,  $\text{CaCl}_2\text{O}_4$ ,  $\text{CaHPO}_4$ , or  $\text{Ca}_3(\text{PO}_4)_2$ , etc. Also, barium and calcium borates, silicates, fluorides (740), ferrocyanides, sulphites, chromates, arseniates, iodates—the acids of which will be identified by 966, or during the work for bases. Also, tartrates (645), citrates (640), and salts of other organic acids not described in this work. Concerning Selenates, Tellurites, see 612; Molybdates, 605.

*Digest the precipitate with dilute hydrochloric acid. If a precipitate remains, filter.*

**Residue:**  $\text{BaSO}_4$  (white).

See 822.

Sulphates precipitate lead and strontium salts.

For comparison of the chief reactions, see 822.

**Solution:**  $\text{H}_2\text{C}_2\text{O}_4$ ;  $\text{H}_3\text{PO}_4$  or  $\text{CaH}_4(\text{PO}_4)_2$ , etc.; barium and calcium chlorides; other acids of less frequent occurrence, as indicated above.

Add ammonium hydroxide to a slight alkaline reaction.

**Precipitate:**  $\text{CaC}_2\text{O}_4$ ,  $\text{CaHPO}_4$ , etc.

Add acetic acid to a distinctly acid reaction.

**Residue:**  $\text{CaC}_2\text{O}_4$  (white).

See 655.

Preliminary examination for acids, 966, Test I., Result 1.

**Solution:**  $\text{H}_3\text{PO}_4$ ,  $\text{CaH}_4(\text{PO}_4)_2$ , etc. (761).

Test by molybdate, as directed in 768. See 79.

The deportment of  $\text{H}_2\text{AsO}_4$  in this table resembles that of  $\text{H}_3\text{PO}_4$ , and is liable to be mistaken for it.

\* For Sulphuric acid, the reaction may be acid; for oxalic acid, the solution may have acetic acidulation; but for phosphoric acid it must not have an acid reaction. Acidity should be neutralized by ammonium hydroxide, which may be added in slight excess.



968. EXAMINATION OF SOME OF THE ACIDS PRECIPITATED BY SILVER NITRATE.

*To the neutral or slightly acid solution,\* add silver nitrate.*

**Precipitate:** Silver salts of a very large number of acids, including those in the residue next below, together with silver carbonate, sulphide, tartrate, and other precipitates dissolved by nitric acid (409).

*Digest with dilute hot nitric acid.*

**Residue:**  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{AgCN}$ ,  $\text{AgIO}_3$ ,†  $\text{AgBrO}_3$ ,  $\text{AgCNS}$ .

Add Ammonium Hydroxide to a strong alkaline reaction (921)

**Residue:**  $\text{AgI}$ , indicating Iodides.

*Test the original solution for iodides, by chlorine-water with carbon disulphide (or starch), as directed in 902 and 928. Follow the Table at 918, and consult the text at 920, 938, and 907.*

**Solution:** Ammonium silver compounds, representing  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HCN}$ ,  $\text{HBrO}_3$ ,  $\text{HIO}_3$ ,  $\text{HCNS}$ .

*Add dilute nitric acid to a slight acidulation.*

**Precipitate:**  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgCN}$ ,  $\text{AgIO}_3$ ,  $\text{AgBrO}_3$ ,  $\text{AgCNS}$ .

<i>Test the original solution for chloride.</i> <i>By distillation for chromium dioxide dichloride (845).</i> <i>By the solubilities of the silver precipitate in ammonium hydroxide and carbonate (843).</i>	<i>Test the original solution for bromide, as directed in 873 and in 920.</i>	<i>Test the original solution for iodate, by reducing agents (911), and by precipitations (918).</i> <i>Test the original solution for bromate, as directed in 881.</i>	<i>Test the original solution for cyanide, 681 or 682.</i> <i>Test the original solution for thiocyanate, by 700. Observe 701.</i>
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Follow the Table of Comparative Reactions, at page 274.

\* If alkaline, the solution should be neutralized by nitric acid. Should effervescence result, boil until it is complete. Should a precipitate form, remove it by filtration.

† By repeated digestion with  $\text{HNO}_3$  the  $\text{AgIO}_3$  may all be dissolved.

## SOLUBILITIES OF THE SALTS OF EACH ACID.

**969.** Concerning salts insoluble in water, it is stated by what *acids* they are **transposed**, and from this it will be seen by what acids they may be dissolved, *i.e.*, changed to compounds soluble in water. As to the solution of salts insoluble in water (and acids) by decomposition with *alkalies*, see 823. For more specific statements as to decomposing and dissolving agents, refer to the descriptions of the acids in question in the text.

**Acetates.** *All soluble in water*; Silver and Mercurous are sparingly soluble.

**Arsenates.** Closely resemble the (ortho)phosphates, both in solubilities and in transposition with acids.

**Arsenites.** *Those of the Alkali bases are soluble.* Those of Barium and Strontium, sparingly soluble; the others are insoluble in water, but *transposed by dilute acids*.

**Borates.** *Only those of the Alkali bases are freely soluble in water*; many of the others being slightly soluble. They are *transposed by all acids, except carbonic*. Some of the metals form non-normal borates.

**Bromates.** *All soluble in water*; Silver, Lead, and Mercurous, sparingly soluble.

**Bromides.** Silver, Lead, and Mercurous, insoluble; Mercuric, sparingly soluble; Bismuth, instable; *all others soluble in water*. The bromides insoluble in water are *scarcely transposed with sulphuric acid, or with dilute nitric acid* (693).

**Carbonates.** *Those of the Alkali bases only are soluble in water.* The acid carbonates less abundantly than the normal. Most of the others are made slightly soluble by free carbonic acid. Carbonates are *transposed by all acids*, except hydrosulphuric and hydrocyanic. The pseudo-triads do not form carbonates; some other heavy metals form basic carbonates in the wet way.

**Chlorates.** *All soluble in water.* Potassium chlorate but moderately soluble.

**Chlorides.** Silver and Mercurous, insoluble; Lead, slightly soluble; *all others soluble in water*; antimonious, stannous and bismuth, soluble in acidulated water.

**Chromates.** Those of the bases of the Alkalies, and Magnesium, Calcium, and Zinc, are soluble in water; Strontium and Mercuric, sparingly soluble; nearly all others insoluble. Iron, Manganese, and Copper form chromates not normal—some of which are soluble in water, but chiefly instable in solution.

**Citrates.** Those of the Alkali bases are freely soluble in water; of Iron, Copper, and Zinc, moderately soluble; *the other (single) citrates, mostly insoluble*; the double citrates mostly soluble. The insoluble citrates are *transposed by dilute mineral acids*.

**Cyanides.** *Mostly insoluble in water*; except those of the Alkali and Alkaline earth metals, and *double cyanides* containing these. Barium cyanide is sparingly soluble. Cyanides are *transposed by nearly all acids*, even when dilute.

**Ferricyanides.** Those of the *Alkali and Alkaline earth bases are soluble* in water; that of Barium, sparingly. A considerable number of the others are insoluble in water, and certain of the bases do not form ferricyanides. See 693. They differ as to *transposition* with acids, but those insoluble are transposed by alkalies.

**Ferrocyanides.** Those of the *Alkali bases and of Magnesium, Calcium* (not the potassio calcium), and Strontium are soluble in water. See 689. Those insoluble differ as to transposition by acids, but are transposed by alkalies.

**Fluorides.** *Those of the Alkali bases are freely soluble in water*; those of the Alkaline

earth metals insoluble ; of Copper, Bismuth, Cadmium, Ferrium, and Zinc, sparingly soluble ; Silver, Tin, and Mercuric, soluble. The insoluble fluorides are *transposed* by strong sulphuric acid, and less easily by hydrochloric and nitric acids.

**Hypochlorites.** *All soluble in water.* (Decomposed by all acids.)

**Hypophosphites.** *All soluble in water.* (Decomposed by nearly all acids.)

**Iodates.** Only those of the *Alkali bases* are *freely soluble*; the others insoluble, or sparingly soluble. Calcium, sparingly soluble ; Barium, Silver, and Lead, insoluble. *Transposed* by moderately dilute mineral acids—those of Silver and Lead by nitric acid not dilute.

**Iodides.** Silver, Lead, Mercurous, Mercuric (and Palladous), *insoluble* in water. Bismuth, and to some extent Copper iodides, are decomposed by water without solution. The others are soluble. The insoluble Iodides are *transposed* with difficulty, or not at all, by sulphuric acid or nitric acid. (894.)

**Nitrates.** *All soluble in water.*

**Nitrites.** *All soluble in water*; Silver, sparingly.

**Nitrophenates.** *All soluble in water*; Potassium, Ammonium, and Lithium, very sparingly ; most others, more freely.

**Oxalates** of the Alkali bases are soluble; Chromium and Stannic oxalates, soluble ; Magnesium and Ferric oxalates, sparingly soluble; the others chiefly insoluble or slightly soluble. *Transposed* by sulphuric, hydrochloric, and nitric acids, not by acetic.

**Permanganates.** *All soluble in water*; Silver, sparingly. A number of the bases decompose the acid radical.

**Phosphates(ortho-).** Of the di- and tri-metallic salts, *only those of the ordinary Alkali bases* are *soluble in water.* (Lithium, insoluble.) Those two-thirds hydric ("acid phosphates") are all soluble in water, to some extent. Acetic acid *transposes* most of the insoluble phosphates, except those of Iron, Aluminium, and Lead; and dilute hydrochloric, nitric, and sulphuric acids transpose all phosphates (partly or wholly, 761).

**Pyrophosphates** are *insoluble* in water, except those of the common Alkali bases. They are scarcely at all *transposed* by acetic acid, but yield their bases to the stronger acid radicals.

**Metaphosphates** of the common Alkali bases, only, are soluble in water. They are not *transposed* with acetic acid, and some of them not readily by other acids when dilute.

**Silicates.** *Those of the Fixed Alkali bases, only, are soluble* in water. These, in solution, are *transposed* by all acids. Of the silicates insoluble in water, many are *transposed* with hydrochloric or sulphuric acid, but the larger number of the natural silicates resist acids. All are decomposed by hydrofluoric acid, and by the fixed alkalis.

**Sulphates.** Those of Barium, Lead, Strontium, Calcium, are insoluble in water, the last-named being slightly soluble. Argentic and Mercurous sulphates are sparingly soluble. Mercuric, Antimonious, and Bismuth sulphates require acidulated water for solution. *All others are soluble in water.* Sulphates are not *transposed* with acids, at ordinary temperatures.

**Sulphites.** *Those of the Alkali bases are soluble*; all others *insoluble*, or very sparingly soluble in water. Those of the Alkaline earth metals are somewhat soluble in

solution of sulphurous acid. All sulphites are *transposed* by acetic and the mineral acids.

**Sulphides.** Of the bases of the Alkalies and Alkaline earths, soluble; the others insoluble in water. The earth metals do not form sulphides. Sulphides of the third-group metals are transposed with dilute acids; those of the second group metals (except Mercury), transposed or decomposed by hydrochloric, nitric, and sulphuric acids.

**Thiocyanates.** Those of Alkali and Alkaline earth bases, and of Iron, Manganese, Zinc, Cobalt, and Copper, are *soluble* in water. Mercuric, sparingly soluble. The others are *transposed* by dilute acids.

**Tartrates.** Those of the Alkali bases are soluble in water, the acid tartrates of Potassium, Ammonium, Rubidium, and Cæsium but sparingly soluble. Manganous, Ferric, Cobalt, Stannous, and Antimonious tartrates are soluble; Calcium tartrate, slightly soluble. The other tartrates, not soluble in water, are mostly somewhat soluble in solution of tartaric acid, and mostly soluble in solutions of Alkalies (as double tartrates); also *transposed* by the mineral acids.

**Thiosulphates.** *All soluble in water*; those of Barium, Lead, and Silver sparingly soluble in water, but made soluble as double salts. *Decomposed by all acids*, 786.





## REAGENTS.\*

[Aq. =  $\text{H}_2\text{O}$  as crystallization water.]

- 971. Acid, Acetic,  $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ .** Sp. grav. 1.04. 30 p.c. acid.  
**Hydrochloric,  $\text{HCl}$ .** Sp. grav. 1.12. 24 p.c. acid.  
**Hydrosulphuric,  $\text{H}_2\text{S}$ .** Water saturated with the acid (777).  
**Hydrofluosilicic,  $(\text{HF})_2\text{SiF}_4$ .** (741.)  
**Nitric,  $\text{HNO}_3$ .** Sp. grav. 1.2 (32 p.c. acid).  
**Nitro-hydrochloric,  $\text{NOCl}_2 + \text{Cl}$ .** About one part of concentrated Nitric to 3 parts of Hydrochloric acid.  
**Nitrophenic,  $\text{HC}_6\text{H}_2(\text{NO}_2)_3\text{O}$ .** (728.)  
**Oxalic,  $\text{H}_2\text{C}_2\text{O}_4$ .** 2 aq. Crystals dissolved in 10 parts of water.  
**Sulphuric,  $\text{H}_2\text{SO}_4$ .** Concentrated, sp. grav. 1.843.  
**Tartaric,  $\text{H}_2(\text{C}_4\text{H}_4\text{O}_6)$ .** Crystals dissolved in 3 parts of water.
- Chlorine-Water,  $\text{Cl}$ .** Water saturated with chlorine (833).  
**Alcohol,  $\text{C}_2\text{H}_5\text{O}$ .** Sp. grav. .815. About 95 p.c.  
**Ammonium Chloride,  $\text{NH}_4\text{Cl}$ .** One part crystallized salt in 8 parts of water.  
**Ammonium Carbonate,  $(\text{NH}_4)_2\text{CO}_3$ .** One part of crystallized salt in 4 parts water, with one part of solution of Ammonia. As a solvent for arsenious sulphide, the reagent is prepared without the addition of solution of ammonia,  $(\text{NH}_4)_4\text{H}_2(\text{CO}_3)_3$ .  
**Ammonium Hydroxide,  $\text{NH}_4\text{OH}$ .** Sp. grav. .96. 10 p.c.  $\text{NH}_3$ .  
**Ammonium Molybdate,  $(\text{NH}_4)_2\text{MoO}_4$ .** Solution in Nitric acid.  
**Ammonium Sulphide,  $(\text{NH}_4)_2\text{S}$ ,** colorless;  $(\text{NH}_4)_2\text{S}_2$  or  $\text{NH}_4\text{HS}$ , yellow; solution of ammonia, treated with hydrosulphuric acid.  
**Ammonium Oxalate,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ .** One part of the crystallized salt (aq.) in 24 parts of water.  
**Barium Chloride,  $\text{BaCl}_2$ .** One part of the crystallized salt (2 aq.) to 10 parts of water.  
**Barium Carbonate,  $\text{BaCO}_3$ .** (103.)  
**Barium Hydroxide,  $\text{Ba}(\text{OH})_2$ .** A saturated water solution (88).  
**Barium Nitrate,  $\text{Ba}(\text{NO}_3)_2$ .** One part to 15 of water.  
**Calcium Chloride,  $\text{CaCl}_2$ .** One part salt (6 aq.) dissolved in 8 parts of water.  
**Calcium Hydroxide,  $\text{Ca}(\text{OH})_2$ .** A saturated water solution (131), also the dry solid.

\* In the greater number of cases, reagents should be "chemically pure." Different uses require different degrees of purity. An article of sodium hydroxide contaminated with chloride may be used in some operations; not in others. Those who have had training in analysis can do without specific directions, which cannot be made to cover all circumstances; and the beginner must depend on others for the selection of reagents.

**Calcium Sulphate,  $\text{CaSO}_4$ .** A saturated water solution (88).

**Carbon Disulphide,  $\text{CS}_2$ .** (873.)

**Cobaltous Nitrate,  $\text{Co}(\text{NO}_3)_2$ .** One part crystallized salt (5 aq.) dissolved in 8 parts of water.

**Copper Sulphate,  $\text{CuSO}_4$ .** One part of the crystallized salt (5 aq.) in 8 parts of water.

**Ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ .** Sp. grav. not over .728—containing not over 5 p.c. alcohol.

**Ferrous Sulphate,  $\text{FeSO}_4$ .** One part crystallized (7 aq.) in 5 parts of water.

**Ferric Chloride,  $\text{Fe}_2\text{Cl}_6$ .** One part of the solid salt (6 aq.) to 15 parts of water.

**Gold Chloride,  $\text{AuCl}_3$ .** Prepared by dissolving pure gold—which may be obtained by precipitation with Oxalic acid—in nitro-hydrochloric acid, evaporating to dryness on the water-bath, and dissolving in water.

**Lead Acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ .** One part of the crystallized salt (3 aq.) dissolved in 10 parts of water.

**Magnesium Sulphate,  $\text{MgSO}_4$ .** One part of the crystallized salt (7 aq.) to 10 parts of water.

**Mercuric Chloride,  $\text{HgCl}_2$ .** One part of the crystallized salt in 16 parts of water.

**Mercurous Nitrate,  $\text{Hg}_2(\text{NO}_3)_2$ .** One part of the crystallized salt (2 aq.) dissolved in 20 parts of water, acidulated with one part nitric acid, or prepared by dissolving mercury.

**Palladous Chloride,  $\text{PdCl}_2$ .** One part of the salt to 20 of water.

**Potassium Chromate,  $\text{K}_2\text{CrO}_4$ .** One part dissolved in 10 parts of water.

**Potassium Dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ .** One part dissolved in 10 parts of water.

**Potassium Chlorate,  $\text{KClO}_3$ .** The crystallized salt.

**Potassium Cyanide,  $\text{KCN}$ .** One part dissolved in 4 parts of water.

**Potassium Ferrocyanide,  $\text{K}_4\text{Fe}(\text{CN})_6$ .** One part of the crystallized salt (3 aq.) dissolved in 12 parts of water.

**Potassium Ferricyanide,  $\text{K}_3\text{Fe}(\text{CN})_6$ .** One part dissolved in 12 parts of water.

**Potassium Iodide,  $\text{KI}$ .** One part dissolved in 20 parts of water.

**Potassium Mercuric Iodide.** Nessler's Solution. Dissolve 3.5 grams of **KI** in 10 c.c. of water; dissolve 1.6 grams of **HgCl<sub>2</sub>** in 30 c.c. of water; add the mercury solution gradually, and with constant stirring, to the potassium iodide solution, until the precipitate ceases to be redissolved; then add 60 c.c. Potassium hydroxide solution and filter. Keep in small bottle, well stoppered.

**Potassium Nitrate,  $\text{KNO}_3$ .** The crystallized salt.

**Potassium Metantimonate,  $\text{KSbO}_3$ .** (514.)

**Potassium Thiocyanate,  $\text{KCNS}$ .** One part dissolved in 12 parts of water.

**Potassium Hydrogen Sulphate,  $\text{KHSO}_4$ .**

**Potassium Sulphate,  $\text{K}_2\text{SO}_4$ .** One part dissolved in 12 parts of water.

**Platinic Chloride,  $\text{PtCl}_4$ .** One part to 10 parts of water. Also prepared by dissolving the scrap-metal in nitro-hydrochloric acid, and purifying by precipitation with ammoniac chloride, dissolving again in the same acid, and evaporating to dryness.

**Sodium Acetate,  $\text{Na}(\text{C}_2\text{H}_3\text{O}_2)$ .** One part crystallized salt (3 aq.) to 5 of water.

**Sodium Carbonate,  $\text{Na}_2\text{CO}_3$ .** The dry salt. Also a solution of the crystals (10 aq.) in 5 parts of water.

**Sodium Diborate,  $\text{Na}_2\text{O}(\text{B}_2\text{O}_3)_2$ .** The crystallized salt (10 aq.), or dried.

**Sodium Hydroxide, NaOH.** Solution in 9 parts of water.

**Sodium Thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .** (Hyposulphite.) One part of the salt in 40 parts of water.

**Sodium Hypochlorite, NaClO.** Agitate one part of good bleaching-powder with ten parts of water; add solution of sodium carbonate as long as a precipitate is formed; allow the solid matter to subside, and siphon off.

**Sodium Phosphate,  $\text{Na}_2\text{HPO}_4$ .** (Disodium hydrogen phosphate.) One part of the crystallized salt (12 aq.) in 10 parts of water.

**Sodium Phosphomolybdate.** (604.)

**Sodium Sulphide,  $\text{Na}_2\text{S}$ .** One part of the solution of soda saturated with Hydrosulphuric acid, to one part unchanged soda solution.

**Sodium Sulphite,  $\text{Na}_2\text{SO}_3$ .** One part of the salt to 5 parts of water.

**Silver Nitrate,  $\text{AgNO}_3$ .** One part crystallized salt in 20 parts of water.

**Stannous Chloride,  $\text{SnCl}_2$ .** One part of the crystallized salt (2 aq.) in 6 parts of water, acidulated with hydrochloric acid (529).

**Strontium Sulphate,  $\text{SrSO}_4$ .** A saturated water solution (88).

**Zinc, Zn.** The granulated metal should be platinized according to 288.

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